CHEMICAL PRODUCTION COMPLEX OPTIMIZATION, POLLUTION REDUCTION AND SUSTAINABLE DEVELOPMENT

A Dissertation

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DEDICATION

To Li Zhu, my beautiful wife and best friend. Thank you for your love, understanding and encouragement.

To my parents, who are the best of examples for their children:

Zhenwen Xu

Shufang Liang

To my brother, who has contributed so much to my life:

Yimin Xu and his wife, Min Liao.

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ABSTRACT

The objective of this research is to propose, develop and demonstrate chemical production complex optimization to determine the optimal configuration of chemical plants in a superstructure of possible plants. The Chemical Complex Analysis System is a new methodology that has been developed to determine the best configuration of plants in a chemical production complex based on the AIChE Total Cost Assessment (TCA) for economic, energy, environmental and sustainable costs.

All new, energy-efficient, and environmentally acceptable plants using greenhouse gases that can produce potentially commercial products designed with HYSYS were integrated into the chemical complex using the System. The optimum configuration of plants was determined based on the triple bottom line that includes sales, economic, environmental and sustainable costs using the System. From eighteen new processes in the superstructure, the optimum structure had seven potentially new processes including acetic acid, graphite, formic acid, methylamines, propylene and synthesis gas production. With the additional plants in the optimal structure the triple bottom line increased from \$343 to \$506 million per year and energy increased from 2,150 to 5,791 TJ/year.

Multicriteria optimization has been used with Monte Carlo simulation to determine the sensitivity of the optimal structure of a chemical production complex to prices, costs, and sustainable credits/cost. In essence, for each Pareto optimal solution, there is a cumulative probability distribution function that is the probability as a function of the triple bottom line. This information provides a quantitative assessment

of the optimum profit versus sustainable credits/cost, and the risk (probability) that the triple bottom line will meet expectations.

The capabilities of the System have been demonstrated, and this methodology could be applied to other chemical production complexes in the world for reduced emissions and energy savings. With this System, engineers will have a new capability to consider projects in depths significantly beyond current capabilities. They will be able to convert their company's goals and capital into viable projects that meet economic, environmental and sustainable requirements.

CHAPTER I INTRODUCTION

The objective of this research is to propose, develop and demonstrate chemical complex optimization. Chemical complex optimization is determining the optimal configuration of chemical plants in a superstructure of possible plants. The objective function incorporates economic, environmental and sustainable costs. The superstructure incorporates new plants that can use carbon dioxide (CO_2) as a raw material and that can produce new products from fullerenes and carbon nanotubes. Chemical complex optimization offers a powerful tool for plant and design engineers to convert their company's goals and capital to viable profits that meet economic, environmental and sustainable requirements.

This chapter introduces the general information of chemical complex optimization and economic, environmental and sustainable costs. The relationship of sustainable development and Responsible Care and that of greenhouse gases and climate change will be discussed in detail.

A. An Overview of Chemical Complex Optimization

The chemical industry is an inseparable part of the U. S. economy and has a positive balance of the trade with more than 70,000 diverse products from various raw materials (Pellegrino, 2000). The growth and productivity are under increasing pressure from economic, environmental and sustainable development constraints. Chemical complex optimization emerges as the times requires, combining economic, environmental and sustainable costs to solve a mixed integer nonlinear programming (MINLP) problem for the best configuration of plants. Chemical company's goal and capital are converted into viable projects which are profitable and meet environmental and sustainable requirements, and also perform evaluations for impacts associated with greenhouse gases, finite resources, and so on. Chemical complex optimization can be employed by these projects and evaluations to help demonstrate that plants are delivering environmental, social and business benefits that will help ameliorate command and control regulations.

B. Introduction of Economic, Environmental and Sustainable Costs

Kohlbrand (1998) described that the companies' activities are changing with movement of business focus from a regional to a global basis. At the same time the chemical industry is moving from end-of-pipe waste treatment to source reduction, recycle and reuse. He gave an example that the cost associated with meeting environmental regulations represented an average of 3% of sales.

Pollution prevention is becoming a critical business opportunity instead of an environmental cost. Tools such as Total Cost Assessment (TCA), Life Cycle Analysis (LCA), eco-efficiency and sustainable development have not developed as quickly in the past two decades as has the opportunity to apply them (Kohlbrand, 1998). They proved ways to develop a balance of safety, reliability, economics, quality, and an acceptable impact on the environment and society for synthesis and improvement of chemical process. The best plant design and product development can be defined by modeling and optimization with multiple objective functions which incorporate economic effects, e.g. costs, yield and long-term cost of ownership, with environmental effects, e.g. life cycle, sustainability and contigent cost analysis (Kohlbrand, 1998).

Chemical complex optimization is used to determine the optimal configuration of chemical plants in a superstructure of possible plants based on existing plants. The objective function incorporates economic, environmental and sustainable costs by the TCA methodology. TCA methodology was presented first by Constable, et al. (2000), and includes five types of costs considered as the criteria for the best economic-environmental design for internal managerial decision making. These five types of costs, respectively, are direct costs for the manufacturing site; potentially hidden corporate and manufacturing site overhead costs; future and contingent liability costs; and external costs (Please refer to Table 2-1 in Chapter II).

Based on TCA, Koch (2001) updated TCA to Total Business Cost Assessment (TBCA) which is used in Dow company (Please refer to Table 2-2 in Chapter 2). They emphasized the future and contingent liability costs, and internal intangible costs when they assessed the total cost with probability for each scenario and then get the best one.

Sustainable development is the concept that development should meet the needs of the present without sacrificing the ability of the future to meets its needs. External costs in TCA, sustainable cost and the triple bottom line are terms that describe the impact of emissions on society. Arthur D Little (2000), a consulting company, presented the business value of sustainable development and the essence of sustainable development for industry.

Sustainable development is said to be an approach to meet stakeholder expectations and develop long term prosperity. The underlying philosophy is meeting today's needs without compromising the ability of future generations to meet their own needs. In fact, a sustainable development approach to business is said to integrate the pursuit of three inter-connected goals, i.e., economic growth, environmental excellence and social responsibility. Companies in ambition-driven growth mode with this approach can grow faster and more profitably through better innovation, greater efficiency, staff alignment and motivation, while preserve the long-term viability of that growth for everyone affected. In addition, Arthur D Little's report says that the triple bottom line in business consists of corporate responsibility, economic and environmental issues. Its idea is that businesses should account for their performance on economic, environmental and social criteria, and attempt to satisfy their stakeholders on all three sets of criteria. More companies are seeking opportunities to meet their customers' desires to be more environmentally and socially responsible without sacrificing the bottom line. Meanwhile, Arthur D Little (2000) combined sustainable development with eco-efficiency that will be reviewed in next chapter, and concluded that three dimensions of sustainable development are economic growth, environmental quality, and social and ethical responsibility.

C. Sustainable Development and Responsible Care

Sustainable development is different from the Responsible Care program which was developed by the American Chemistry Council (ACC) formerly the Chemical Manufactures Association (CMA) to help overcome the chemical industry's public image of ruthless, uncaring ambition to one of trust, honesty and credibility (Reisch, 2001). There was a discussion on sustainability among several experts (Reisch, 2001). Paul Reeve, executive director of UKCIA’s (the Chemical Industries Association of the U. K.) Responsible Care program, says that Responsible Care exists within sustainable development as an important initiative and has its social aspects where worker safety and health are concerned, but without addressing the broad social agenda being part of sustainable development. Also Garrity Baker, senior director of international affairs at American Chemistry Council (ACC), points out “Responsible Care is about how we should conduct ourselves. The notion that sustainable development allows different actors in society to rally together”.

There are some other different opinions on the relationship between sustainable development and Responsible Care. Sebastian Beloe, a director of London-based SustainAbility, states that sustainable development is about new products, new systems, and massively reducing the environmental impacts of goods and services vs the Responsible Care that is a defensive program all about managing threats (Reisch, 2001). Watkins (2002) raised that the chemical industry’s commitment to Responsible Care has paved the way for progress on sustainability even though they are different. Dupont (Watkins, 2002) believes that these two are different since Responsible Care challenges a company to do its best with the technology it has without challenging companies to create “real green” products and processes. BASF (Watkins, 2002) deems that Responsible Care is an integral part of sustainable development and it has nailed down the environmental part of three key components of sustainable development, i.e. economic, environmental and social development.

Along with sustainable development, eco-efficiency, which is the extent to which economic development and ecological impacts are balanced, appears to emphasize the relationship between producing and ecosystem. Meanwhile, in order to get sustainable development, green chemistry and green chemical engineering are coined closely. Sustainability metrics and Sustainable Process Index (SPI) are the two important methods to measure the sustainability. Emission-trading system for greenhouse gases is an important way to get sustainability according to Kyoto Protocol (Bolin and Kheshgi, 2001).

D. Greenhouse Gas and Climate Change

The relationship between greenhouse gases and climate changes has been studied for a long time (IPCC, 1995, 1996a, 1996b, 2001; National Research Council, 2001a). People have got to know that greenhouse gases can induce global climate warming and emissions should be reduced, especially for CO_2 emissions.

D-1. Greenhouse Gases Introduction

Global warming first emerged when scientists become aware of the amount of carbon dioxide being added to the atmosphere as a result of human activity. Jean-Baptiste Joseph Fourier, a French scientist, discovered the greenhouse effect and John Tyndall, an Irish physicist, measured the radiation absorption efficiencies of various gases, a measure of their effectiveness as greenhouse gases. He was concerned that a decrease in atmospheric CO_2 could lead to another ice age.

The temperature of the earth is strongly influenced by the existence, density and composition of its atmosphere. The components of the earth's atmosphere that trap radiation are called "greenhouse gases". All greenhouse gases absorb infrared radiation at particular wavelengths. The sun furnishes the earth with a generous amount of ultraviolet, visible, and infrared radiation because it radiates at 6,000 ºC. The earth in turn radiates some of the sun's energy back into space at a very low temperature, about 15 ºC. Because of this low temperature, nearly all of the earth's radiation is in the low-energy infrared region. The greenhouse gases absorb the radiation both entering the earth's atmosphere and being emitted by the earth itself, causing the earth to heat up. There are multiple greenhouse-related gases, including water vapor (H_2O), carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), odd nitrogen compounds, the chlorofluorocarbons and their replacement, and aerosol compounds.

The Kyoto Protocol instituted legally binding emission levels on six greenhouse gases, i.e. CO_2, CH_4, N_2O, HFCs (hydrofluorocarbons), PFCs (perfluorocarbons), SF_6 (sulfur hexafluoride) (Table 1-1). The atmospheric concentration of water vapor is nearly one percent that is larger than less than 0.04 percent of carbon dioxide. Water vapor is most common, but the effect of human activity on global water vapor concentration is considered negligible. In addition the anthropogenic emissions of water vapor are not factored into national greenhouse gas emission inventories to meet the United Nations Framework Convention on Climate Change (UNFCC) or the Kyoto Protocol.

Table 1-1 Global Warming Potentials (GWP) and Atmospheric Lifetimes (Years)

Gas	Atmospheric Lifetime	1996 GWP[a]	2001 GWP[a]
Carbon dioxide (CO_2)	50-200	1	1
Methane (CH_4)[b]	12±3	21	23
Nitrous oxide (N_2O)	120	310	296
HFC-23	264	11,700	12,000
HFC-125	32.6	2,800	3,400
HFC-134a	14.6	1,300	1,300
HFC-143a	48.3	3,800	4,300
HFC-152a	1.5	140	120
HFC-227ea	36.5	2,900	3,500
HFC-236fa	209	6,300	9,400
HFC-4310mee	17.1	1,300	NA
CF_4	50,000	6,500	5,700
C_2F_6	10,000	9,200	11,900
C_4F_{10}	2,600	7,000	NA
C_6F_{14}	3,200	7,400	NA
SF_6	3,200	23,900	22,200

Source: IPCC's (The Intergovernmental Panel on Climate Change) second assessment report (1996b) & IPCC's third assessment report (2001)
a 100 year time horizon
b The methane GWP includes the direct effects and those indirect effects due to the production of tropospheric ozone and stratospheric water vapor. The indirect effect due to the production of CO_2 is not included.

Referring to Table 1-1, carbon dioxide is the most important human-released greenhouse gas from the perspective of potential changes in future climate. Its principle source of emission is fossil fuel use. The worldwide CO_2 emissions from the consumption and flaring of fossil fuels in 1991 are listed in Table 1-2 where only the countries with CO_2 emissions over 100 million metric tons carbon equivalent are listed. Land-change in general and deforestation in particular play important roles. Also greenhouse gases have natural sources. They come from volcanic eruptions, ocean evaporation, and animal and plant respiration.

Table 1-2 World Carbon Dioxide Emissions from the Consumption and Flaring of Fossil Fuels in 1999, from EIA (2002) (Unit: Million Metric Tons Carbon Equivalent)

Country	CO_2 emissions	Country	CO_2 emissions
Canada	153	United States	1,526
France	109	Germany	223
Italy	113	United Kingdom	144
Russia	440	Ukraine	105
South Africa	105	China	792
India	240	Japan	307
South Korea	105	World Total	6,323

In the early 1960s the concentrations of carbon dioxide and several other greenhouse gases in the earth's atmosphere increased every year. The data from 1990 to 2000 are listed in Table 1-3 by gas, and in Table 1-4 based on global warming potential. Also Figure 1.1 corresponds to Table 1-4. In Table 1-2 and Table 1-4, Carbon equivalent is a metric measure used to compare emissions of different greenhouse gases based on their global warming potential (GWP). GWPs are used to convert greenhouse gases to CO_2 equivalents, and then they can be converted to carbon equivalents by multiplying by 12/44 (the ratio of the molecular weight of carbon to carbon dioxide). So the postulation of that increasing concentration of greenhouse gases would make the earth warmer was put forward, based on that current concentrations of greenhouse gases keep the earth at its present temperature (EIA, 2001). Computer-based simulation models produced similar results that an increase in concentrations of greenhouse gases would cause an increase in global temperature, which leads the weather change, the rising of oceans level and other disruptive phenomena (EIA, 2001). However, it is still very difficult to discover human impact on climate from normal temporal and spatial variations in temperature on a global

Table 1-3 Summary of Estimated Greenhouse Gases Emissions in U.S for 1990-2000, from EIA (Energy Information Administration) (2001)
(Unit: Million Metric Tons of Gas)

Gas	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	P2000
Carbon Dioxide	4,969	4,917	5,013	5,130	5,224	5,274	5,455	5,533	5,540	5,631	5,806
Methane	32	32	32	31	31	31	30	30	29	29	28
Nitrous Oxide	1	1	1	1	1	1	1	1	1	1	1
HFCs, PCFs, SF6	*	*	*	*	*	*	*	*	*	*	*

*---Less than 0.05 million metric tons of gas
P---preliminary data

Table 1-4 Greenhouse Gases Emissions Based on Global Warming Potential[a] in U.S. for 1990-2000, from EIA (2001) (Unit: Million Metric Tons Carbon Equivalent)

Gas	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	P2000
Carbon Dioxide	1,355	1,341	1,367	1,399	1,425	1,438	1,488	1,509	1,511	1,536	1,583
Methane	199	200	200	194	194	195	188	186	181	180	177
Nitrous Oxide	94	96	98	98	106	101	101	99	99	100	99
HFCs, PCFs, SF6	30	28	29	30	32	35	39	42	46	45	47
Total	1,678	1,665	1,694	1,721	1,757	1,769	1,816	1,836	1,837	1,861	1,906

a---global warming potential from IPCC (1996b)
P---preliminary data

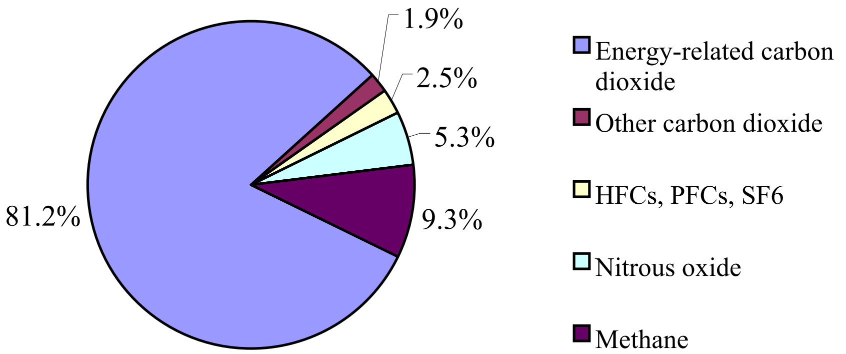


Figure 1.1 Greenhouse Gas Emissions by Gas in U.S., 2000, from EIA (2001)

scale. The Intergovernmental Panel on Climate Change (IPCC) (2001) has stated that, because of the increases in greenhouse gases during the past century, the average global temperature of the earth has increased by $0.6 \pm 0.2°\text{C}$ since the late 19th century.

The National Research Council (2001a) commissioned by the National Academic of Science on the request of Bush Administration gave a review on the IPCC report with some suggestions as follows:

> "Greenhouse gases are accumulating in Earth's atmosphere as a result of human activities, causing surface air temperatures and subsurface ocean temperatures to rise. Temperatures are, in fact, rising. The changes observed over the last several decades are likely mostly due to human activities, but we can not rule out that some significant part of these changes is also a reflection of natural variability. … Because there is considerable uncertainty in current understanding of how the climate system varies naturally and react to emissions of greenhouse gases and aerosols, current estimates of the magnitude of the future warming should be regarded as tentative and subject to future adjustments (either upward or downward)."

While it is uncertain for both the extent and consequences of human-induced global climate change, the threat of climate change has raise the efforts by all of the world to find some methods to limit the risk of global warming. To date, almost all of the efforts focus on the identifying and reducing emissions of greenhouse gases.

In summary, greenhouse gases are getting more attention from the society. Even though the effects are not very clear now, people will regard them as the important factor inducing global climate warming.

D-2. CO_2 Generation

Since CO_2 is the most important greenhouse gas causing global warming, it will be discussed in detail as follows. Its cycle and carbon cycle are first presented in Figure 1.2. The numbers in this figure are the averages for the 1980s estimated by the

Intergovernmental Panel on Climate Change (IPCC) (1995). There are vast reservoirs of carbon in the system that can exchange fairly rapidly with each other. The atmosphere contains about 750 gigatons (1 gigaton = 10^9 tons) of carbon (GtC) as CO_2; the terrestrial biosphere about 550 GtC as CO_2; the soil about 1,500 GtC as CO_2; the mixed layer of the ocean about 1,000GtC as CO_2; and the deep ocean about 38,000 GtC as CO_2. Also there are exchange fluxes of carbon as CO_2 in among these reservoirs. First is the one-way exchange. The human contribution to emissions to the atmosphere from combustion of fossil fuels is about 5.5 GtC as CO_2 per year in the 1980s; estimates of net emissions from tropical deforestation is about 1.6 GtC as CO_2 per year. Second is natural cycle involving two-way exchange of CO_2. CO_2 is exchanged at about 60 GtC per year into and out of the terrestrial biosphere and soil through respiration, photosynthesis and decay, and exchanged at about 90 GtC per year into and out of ocean through the mixed layer.

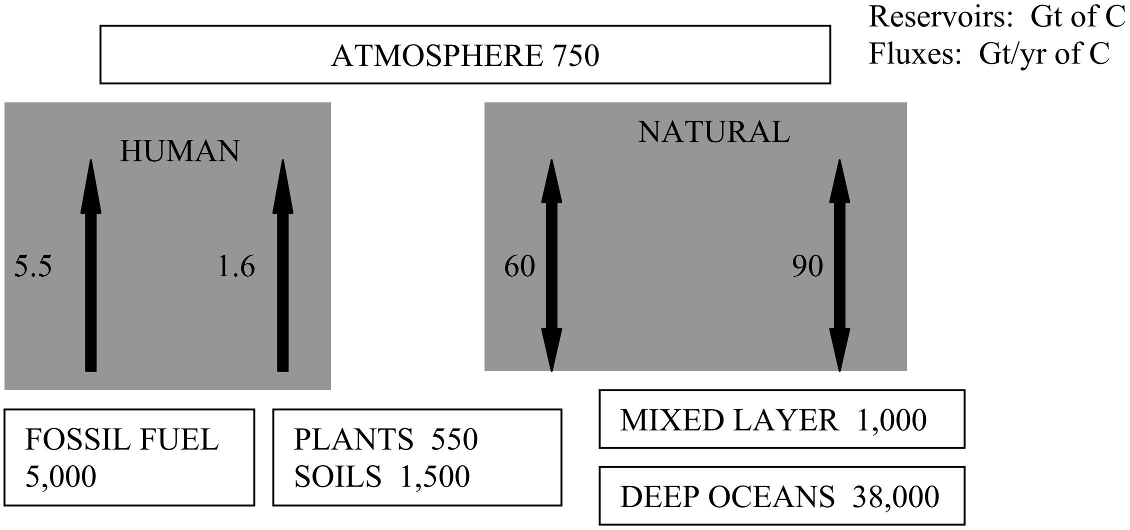


Figure 1.2 The Carbon Cycle, from IPCC (1995)

There are many natural sources of carbon dioxide, including nearly all living species of animals, microbes in the soils, decaying plants and animals after they die, and gaseous emissions from lakes and oceans. The anthopogenic sources are mainly burning of fossil fuels and deforestation. The various natural and human-generated sources are summarized, along with the magnitudes of each in Table 1-5.

Table 1-5 Sources of Carbon Dioxide, from Parsons (1995)

Sources	Value (GtC/Yr)	Percentage (%)
Natural Sources		
Ocean	90	57.29
Plants and Soil	60	38.19
Subtotal	150	95.48
Anthropogenic Sources		
Burning Fossil Fuels	5.5	3.50
Deforestation	1.6	1.02
Total	157.1	100.00

Stringer (2001) stated that in 1995, the carbon emissions of U.S. in million tonnes carbon equivalent (MtC) were 524 MtC for buildings including heating, lighting and so forth, 630 MtC for industry, and 473 MtC for transportation (Figure 1.3). He considered the usual sources for the greenhouse gases.

The EIA (Energy Information Administration) (2001) had a slightly different method to represent the source of carbon emissions. Its report in 2001 gave the main source for the carbon dioxide emissions (Figure 1.1). The main part is the energy consumption related carbon dioxide which comes four general end-use categories, namely residential, commercial, transportation and industrial sector. Emission of each sector is proportional to its electricity consumed and emissions for these four sectors from 1990 to 2000 are displayed in Figure 1.4. There are some rules for the emissions of the sectors. Residential carbon dioxide emissions are influenced by weather, demographic factors, living space attributes, and building shell and appliance efficiency choices. Emissions from the commercial sectors are more affected by economic trends and less affected by population growth than are emissions from the residential sector. Both transportation and industrial emissions are influenced mainly by the economy growth.

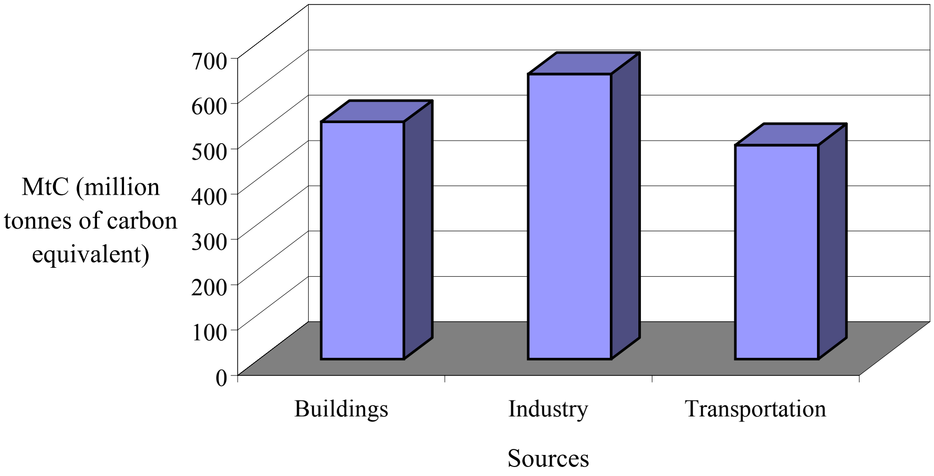


Figure 1.3 U.S. Carbon Emissions Sources in 1995, from Stringer (2001)

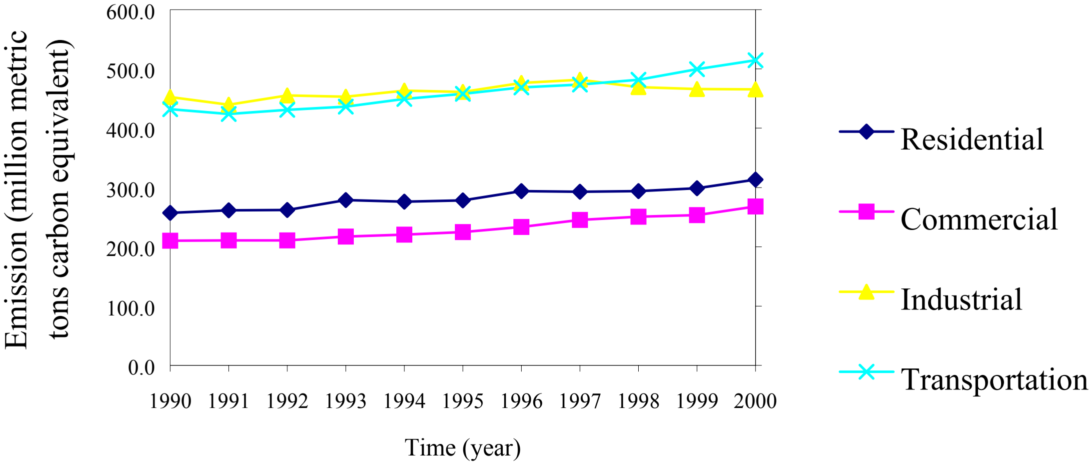


Figure 1.4 U.S. Carbon Dioxide Emissions by Sector, 1990-2000, from EIA (2001)

As shown in Figure 1.5 EIA (2001) stated that there are six industry groups having carbon dioxide emissions totaling 320.1 million metric tons carbon equivalent. Petroleum and coal products were the largest with 87.5 million metric tons of carbon equivalent, followed by chemicals and then all other manufacturing.

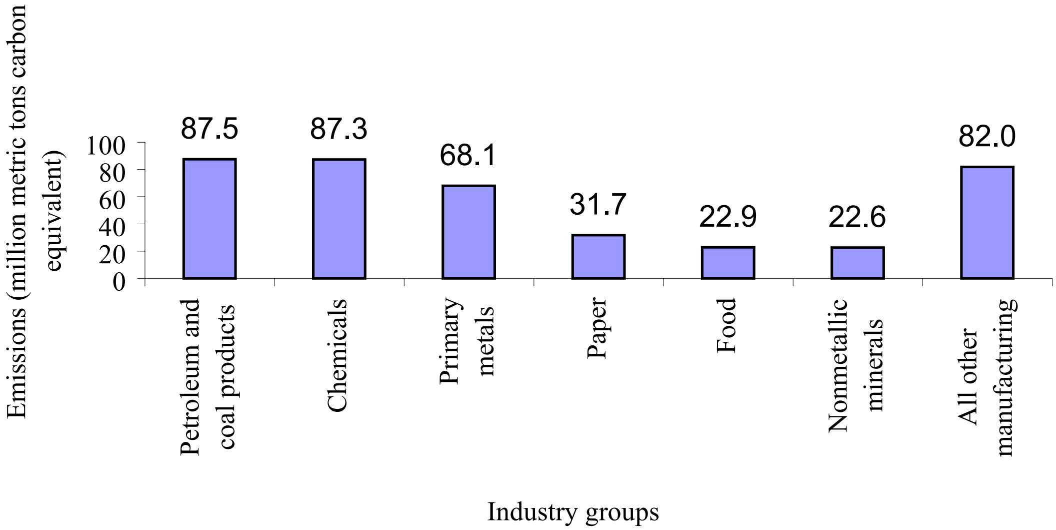


Figure 1.5 Total Energy-Related Carbon Dioxide Emissions for Selected Manufacturing Industries, 1998, from EIA (2001)

Most of the carbon dioxide emitted directly by the petroleum industry, which mainly deals with oil and gas exploration and production, refining and marketing, and petrochemicals, results from the combustion of hydrocarbons. As in Figure 1.6 from McMahon (1999), for BP's about 40 million tonnes of CO_2 emission in 1997, only 3% of the direct carbon dioxide emissions were from process (non-combustion) sources, with the remaining 97% resulting from the combustion of hydrocarbons for internal energy requirements (90%) and flaring (7%). Most of the hydrocarbons burnt are internally generated fuels gas such as in refineries and chemical plants, associated gas from oil and gas production, and liquid residues. The contribution from the combustion of commercially available fuels with known specification is very low within a few percent (McMahon, 1999).

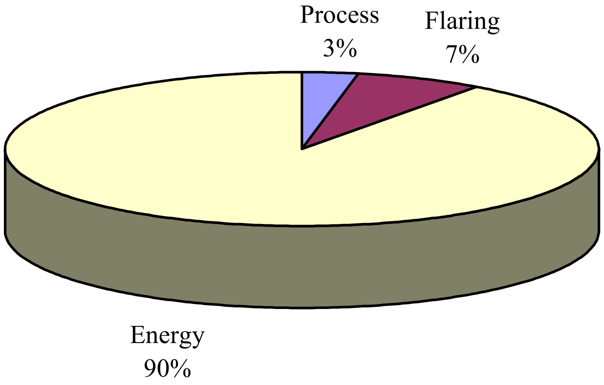


Figure 1.6 Direct Carbon Emissions Split by Sources for BP in 1997,
from McMahon (1999)

In summary, CO_2 is generated in different ways. Basically, it is generated from the nature, but the CO_2 emissions from anthropogenic sources are increasing by 1.6% per year since 1990. The main part of CO_2 emissions in manufacturing industries is from chemical and refinery industry sources, about 174.8 million tonnes carbon equivalent accounting 43.5% of those from manufacturing industries in 1998 (EIA, 2001). This is the reason that CO_2 is considered in sustainable costs.

D-3. Climate Change Analysis and Greenhouse Gas Mitigation

The fact that greenhouse gas emissions can cause climate changes is well known to people. The models dealing with the greenhouse gas emissions mitigation and climate change analysis have emerged as the times require. Since economic efficiency, social equity and environmental protection are the target people pursue, the climate change analysis and greenhouse gas mitigation should be carried on carefully.

Based on a doubling of the preindustrial CO_2-equivalent concentration of all greenhouse gases ($2\times CO_2$), the marginal damage done by one extra ton of carbon emitted is estimated at $5-125 per ton of carbon emitted now. The marginal damage is affected by model assumptions and discount rates. The economic effects occurring at different times can be compared using the discount rates. For example, there are two approaches for discount rate for climate change analysis (IPCC, 1996a). The prescriptive approach is from the normal or ethical perspective, beginning with the question, “How ethically should impacts on future generation be valued?” The descriptive approach is from positive perspective, beginning with the question, “What choices involving trade-offs across time do people actually make?” and, “To what extent will investment made to reduce greenhouse gas emissions displace investments elsewhere?” The prescriptive approach has relatively low discount rates and more spending on climate change mitigation, but the description approach has higher discount rates and less spending on climate change mitigation.

For decision-making of climate changes modern benefit-cost analysis provides an analytical framework that can compares the consequences of alternative policy actions on a quantitative basis. There are uncertainties in each link in the causality chain of climate changes (Figure 1.7), which greatly amplifies the total uncertainty in the extent of damages caused by climate change (IPCC, 1996a).

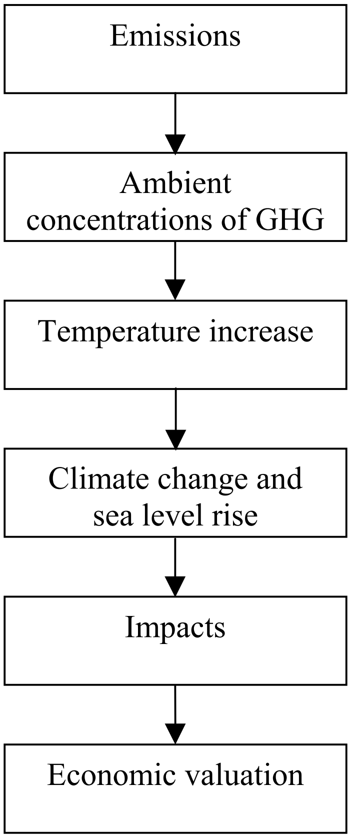


Figure 1.7 The Causality Chain, from IPCC (1996a)

For the damage assessment of social costs of climate change there are three approaches, i.e., benefit-cost approach, sustainability approach and consensus viewpoint approach (IPCC, 1996a). The choice between first two depends on attitude to uncertainty, the degree of concern for the well-being of future generations, and beliefs about the damage function. The third has the common features of the first two.

IPCC (1996a) gave the available policy options to counter greenhouse effects with the possible effects (Figure 1.8). Mitigation options are to reduce emissions, including change demands, new technology, change energy sources and efficiency and conservation. Adaptation options have two types. One is passive adaptation, such as let society adapt. The other is active adaptation, such as change crops and alter land use to decrease vulnerability, and relief or aid and insurance to modify effects. Indirect policy options are for global economic trends, such as reduce population growth, alter resource demands and supply, and change technology.

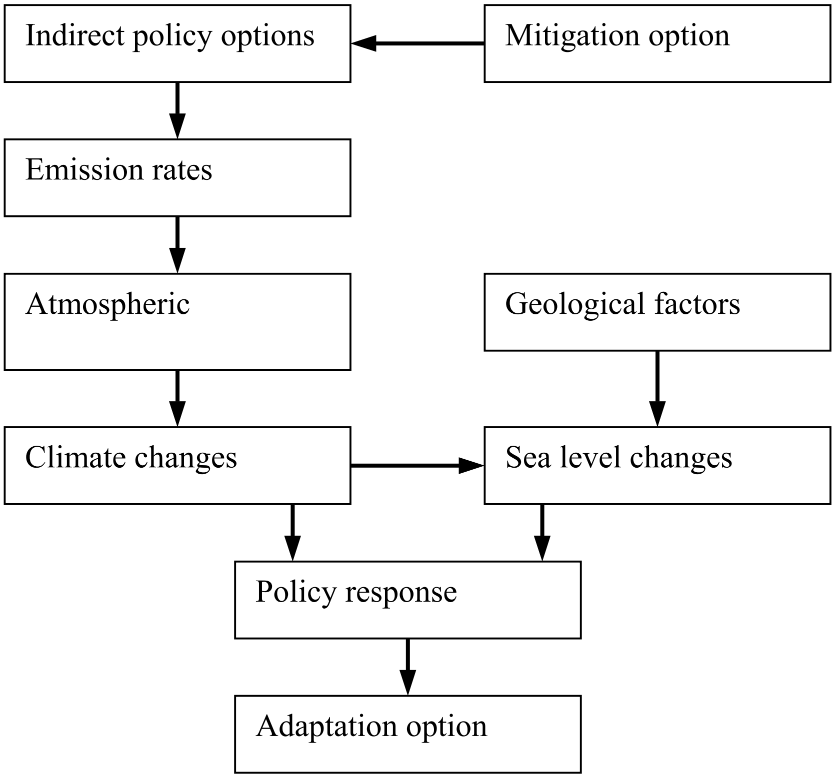


Figure 1.8 Options to Counter Greenhouse Effect and Their Feedback, from IPCC (1996a)

IPCC (1996a) introduced two approaches in energy modeling analysis for estimating the costs of mitigating greenhouse gases. One is called bottom-up, which is analysis and the produced energy system projections. The other is called top-down, which is prepared by governments, the energy industry, and the energy economists relying on extrapolatory approaches to capture the overall economic impact of mitigating greenhouse gases. Bottom-up models rely on the detailed analysis of technical potential, focusing on the integration of technology costs and performance data. However, top-down models analyze aggregated behaviors based on economic indices of prices and elasticities. They started as macroeconomic models which tried to capture the overall economic impact of a climate policy, which was usually in the form of a carbon tax or, more rarely, tradable permits because of the difficulty of assessing other types of policy instruments.

In addition, IPCC (1996a) provided integrated assessment models for climate change, which can be divided into policy optimization models and policy evaluation models. Policy optimization models have three types: benefit-cost models attempt to balance the benefits and costs of climate policies; target-based models optimize responses, given targets for emissions or climate change impacts; uncertainty-based models deal with decision making under conditions of uncertainty. Policy evaluation models can be divided into two types: deterministic projection models where each input and output takes on a single value; stochastic projection models where at least some inputs and outputs are treated stochastically.

For Greenhouse gas mitigation policies should be expressly designed to mitigate global climate change, where the associated policy instruments must be provided. For example, greenhouse policy instruments are divided into domestic and international policies. Domestic policy instruments include conventional regulatory instruments, such as energy efficiency of buildings; market-based instruments, such as taxes, subsidies, and tradable permits; and other complementary policies, such as education and provision. International policy instruments have regulatory instruments, such as uniform standards for emission reduction agreement; international taxes and harmonized domestic taxes; tradable quotas; and other complementary policies, such as technology transfer from industrialized to developing countries (IPCC, 1996a).

For policy assessment IPCC (1996a) presented two important criteria, which are economic efficiency and distributive justice, with the following general set of criteria. They, respectively, are probability that the environmental goal will be achieved; efficiency or cost-effectiveness; dynamic incentives for innovation and the diffusion of improved technologies; flexibility and adaptability to exogenous changes in technology, resource use, and consumer tastes; distributional equity; and feasibility in terms of political implementation and administration.

In summary, there are many ways to analyze the climate change and mitigating greenhouse gases. These methods should continue to be studied to improve their accuracy.

E. Chemical Complexes in the World

There are many chemical complexes in the world. The summary of some of the larger chemical complexes worldwide is in Table 1-6. Chemical complex optimization has huge potential to be applied to these complexes combing economic, environmental and sustainable costs.

F. Summary

The relationship between greenhouse gases and climate changes has been studied for a long time (IPCC, 1995, 1996a, 1996b, 2001; National Research Council, 2001a). The common conclusion is that greenhouse gases can induce global climate

Table 1-6 Chemical Complexes in the World

Continent	Name and Site	Notes
North America	• Gulf coast petrochemical complex in Houston area (U.S.A.)	• Largest petrochemical complex in the world, supplying nearly two-thirds of the nation's petrochemical needs
	• Chemical complex in the Lower Mississippi River Corridor (U.S.A.)	
South America	• Petrochemical district of Camacari-Bahia (Brazil)	• Largest petrochemical complex in the southern hemisphere
	• Petrochemical complex in Bahia Blanca (Argentina)	
Europe	• Antwerp port area (Belgium)	• Largest petrochemical complex in Europe and world wide second only to Houston, Texas
	• BASF in Ludwigshafen (Germany)	• Europe's largest chemical factory complex
Asia	• The Singapore petrochemical complex in Jurong Island (Singapore)	• World's third largest oil refinery center
	• Petrochemical complex of Daqing Oilfield Company Limited (China)	
	• SINOPEC Shanghai Petrochemical Co. Ltd. (China)	
	• Joint-venture of SINOPEC and BP in Shanghai under construction (2005) (China)	• Largest petrochemical complex in Asia
	• Jamnagar refinery and petrochemical complex (India)	
	• Sabic company based in Jubail Industrial City (Saudi Arabia)	
	• Petrochemical complex in Yanbu (Saudi Arabia)	• World's largest polyethylene manufacturing site
	• Equate (Kuwait)	• World's largest & most modern for producing ethylene glycol and polyethylene
Oceania	• Petrochemical complex at Altona (Australia)	
	• Petrochemical complex at Botany (Australia)	
Africa	• petrochemical industries complex at Ras El Anouf (Libya)	• One of the largest oil complexes in Africa

warming and emissions should be reduced, especially for the CO_2 emission. For the composition of emissions for greenhouse gases, CO_2 is the dominant species accounting for 83% of the total emissions (EIA, 2001). CO_2 emissions and utilization are listed in Table 1-7. An overview of CO_2 sources and cycles is provided (IPCC, 1995). There are two sources of CO_2. One is natural sources which is recycled and accounts for 150 GtC per year, such as ocean, plants and soil. The other is anthropogenic sources that adds 7.1 GtC per year to the atmosphere, mainly from the burning of fossil fuels and deforestation (Parsons, 1995).

The CO_2 emissions from the consumption and flaring of fossil fuels in U.S. in 1999 are 1526.12 million metric tons carbon equivalent accounting for 24.1% of worldwide. The carbon emissions from industrial sources of U.S. were 630 million metric tons carbon equivalent, with 524 and 473 million metric tons carbon equivalent from buildings and transportation, respectively (Stringer, 2001). The CO_2 emissions from industrial sector were about 500 million metric tons carbon equivalent per year, similar to those from the transportation and larger than those from residential and commercial sectors (about 300 and 250 million metric tons carbon equivalent per year, respectively) (EIA, 2001).

For the distribution of CO_2 emissions in the manufacturing industries, the petroleum and coal products industry and the chemical industry are 43.5% of the total 402.1 million metric tons carbon equivalent (EIA, 2001). The most important part of direct carbon emissions is 90% from energy (McMahon, 1999). CO_2 emissions from the consumption and flaring of fossil fuels in the world are 6,323 million metric tons carbon equivalent per year (EIA, 2002).

Table 1-7 Carbon Dioxide Emissions and Utilization
(Million Metric Tons Carbon Equivalent Per Year)

CO_2 emissions and utilization		Reference
Total CO_2 added to atmosphere		IPCC (1995)
Burning fossil fuels	5,500	
Deforestation	1,600	
Total worldwide CO_2 from consumption and flaring of fossil fuels		EIA (2002)
United States	1,526	
China	792	
Russia	440	
Japan	307	
All others	3,258	
U.S. CO_2 emissions		Stringer (2001)
Industry	630	
Buildings	524	
Transportation	473	
Total	1,627	
U.S. industry (manufacturing)		EIA (2001)
Petroleum, coal products and chemicals	174.8	
Chemical and refinery (BP)		McMahon (1999)
Combustion and flaring	97%	
Noncombustion direct CO_2 emission	3%	
Agricultural chemical complex in the lower Mississippi River corridor excess high purity CO_2	0.183	Hertwig, et al. (2002)
CO_2 used in chemical synthesis	30	Arakawa, et al. (2001)

In the lower Mississippi River corridor agricultural chemical complex, 0.183 million metric tons carbon equivalent of high purity excess CO_2 per year is vented to the atmosphere (Hertwig, et al., 2002). Hence, the CO_2 available has a huge potential to be reused. Currently about 110 megatons of CO_2 are used annually for the chemical synthesis, such as urea, methanol, salicylic acid, cyclic carbonates and polycarbonates, where urea production is the largest with about 90 megatons in 1997 (Arakawa, et al., 2001).

The next chapter reviews the literature of methods that have been proposed and applied for the reduction of greenhouse gases. Also methods for eco-efficiency, sustainability, green chemistry and engineering will be described.

CHAPTER II LITERATURE REVIEW

In this chapter, industrial applications of industrial ecology, Total Cost Assessment (TCA), sustainable development, eco-efficiency, green chemistry and engineering will be reviewed. Also, carbon dioxide (CO_2) utilization and nanotechnology will be reviewed respectively. Based on this information a Chemical Complex Analysis System will be proposed that uses an economic, environmental and sustainable measure of effectiveness with new technology to determine the best configuration of plants in a chemical production complex. The Chemical Complex Analysis System's capabilities can be demonstrated by application to an existing chemical complex in the lower Mississippi River corridor.

A. Chemical Complex and Industrial Ecology

Integrating notions of sustainability into environmental and economic systems creates industrial ecology, whose key themes are moving from linear throughout to closed-loop material and energy use. Ehrenfeld and Gertler (1997) defined an industrial ecosystem as a complex coming from a set of interrelated symbiotic links among groups of firms in an area and gave the complex at Kalundborg, Denmark as an example. They concluded that using interdependent plants was better than the independent ones.

The characteristics of stable ecological systems are steady-state, entropy-minimizing, highly interdependent collections of producers and customers. Another example of the application of industrial ecosystem concepts is the petrochemical complex located in Houston Ship Channel which is the largest petrochemical complex in the world supplying nearly two-thirds of the nation’s petrochemical needs. The combination of industry and transportation facilities can be considered an industrial ecosystem.

Similarly, the U.S. President's Council for Sustainable Development (PCSD) (1996) gave the definition of eco-industrial parks as an environmental efficient version of industrial parks. They follow a systems design in which one facility's wastes becomes another facility's feedstock, and they ensure that raw materials are recycled or disposed of efficiently and safely. There is a project under way in Chattanooga, Tennessee and in other places. There are barriers and limits to the development of symbiotic communities. For example, exchange of information about nearby industries and their inputs and outputs are often difficult or costly to obtain.

In summary, chemical complexes using industrial ecology are more sustainable and profitable than the separate and independent plants. When these complexes are being designed, the interdependent relationships among the plants in the complexes are needed. To get the optimal configuration of chemical complexes, one of the more important parts in chemical complex optimization is the calculation of total cost, and this is described in the next section.

B. Total Cost Assessment (TCA)

Constable, et al. (2000) gave detailed information about the Total Cost Assessment (TCA, or TCAce) methodology, which is designed for internal managerial decision-making. In TCA the costs are divided into five types which are listed in Table 2-1. When a company must decide between alternative projects, all potential environmental and health costs should be fully considered. TCA methodology provides the framework for estimating baseline costs that have a much broader and potentially longer timeframe. The potential user groups are engineers in the assessment of the environmental projects; business managers and analysts in developing product and business strategy; process and product engineers in the design stage of new products and processes.

Table 2-1 Costs Included in the TCA Methodology, from Constable, et al. (2000)

Cost Type	Definition
Type I: Direct costs for the manufacturing site	Direct costs of capital investment, labor, raw material and waste disposal. May include both recurring and non-recurring costs. Includes both capital and Operations and Management (O&M) costs.
Type II: Potentially hidden corporate and manufacturing site overhead costs	Indirect costs not allocated to the product or process. May include both recurring and non-recurring costs. May include both capital and O&M costs. May include outsourced services.
Type III: Future and contingent liability costs	Liability costs include fines and penalties caused by non-compliance and future liabilities for forced clean-up, personal injury and property damage.
Type IV: Internal intangible costs	These are costs that are paid by the company. Includes difficult to measure cost entities, including consumer acceptance, customer loyalty, worker morale, worker wellness, union relations, corporate image, community relations and estimates of avoided costs – fines, capital, etc.
Type V: External costs	Costs and benefits for which the company does not pay directly. These costs or benefits are realized by society and include deterioration of the environment by pollutant dispersions that are currently in compliance with applicable regulations.

In the past, Type I and Type II costs were used only to determine the profits. Then Type III and Type IV were included, and in last several years Type V costs were considered in different depths. Koch (2001) gave updated information on TCA, named as Total Business Cost Assessment (TBCA), which is used in Dow Company. He agreed that TCA original objective is a modeling tool for better understanding of all costs and benefits associated with environmental health and safety (EH&S) decision making, including direct, indirect, contingent risk, liabilities and externalities. Koch reported some changes in cost type definitions, and he gave new definitions in Table 2-2. Type III and IV are primary focus of the TBCA works and Type I and II costs will be unique to each individual project or opportunity. He used a Monte Carlo simulation method for alternative scenarios and finally obtained the total cost with probability for each scenario. Then he compared them to get the best one. Although he did not use Type V cost in the assessment for lack of the data, he insisted that long term Type V cost be included in the total cost in Dow's TBCA.

Table 2-2 TBCA Types of Benefits/Costs (without Type V Cost), from Koch (2001)

Type	Description/Example	Note
I & II	Conventional economics	Often referred to as the "Hard" economics which have historically been applied
III	Future & contigent liabilities - fines & penalties, legal fees - business interruptions - cost of environmental cleanup - cost to discharge wastewater	Often referred to as the "Soft" economics which have NOT been historically translated to economic units
IV	Intangible internal costs - corporate image - public perception	

In order to consider industrial costs thoroughly, Norris (2001) proposed integrating Life Cycle Cost (LCC) analysis and Life Cycle Assessment (LCA). The differences between LCA and LCC are given in Table 2-3, which lead to their different utilizations, i.e. providing answers to different questions. LCA evaluates the environmental performance of the product systems and considers all causally

Table 2-3 Difference between LCA and LCC, from Norris (2001)

Tool and Method	LCA	LCC
Purpose	Compare relative environmental performance of alternative product systems for meeting the same end-use function. Do this from a broad, societal perspective	Determine cost-effectiveness of alternative investments and business decisions, from the perspective of an economic decision maker such as a manufacturing firm or a consumer
Activities which are considered part of the "Life Cycle"	All processes causally connected to the physical life cycle of the product; including the entire pre-usage supply chain; use and the processes supplying use; end-of-life and the processes supplying end-of-life steps	Activities causing direct costs or benefits to the decision maker during the economic life of the investment, as a result of the investment
Flows considered	Pollutants, resources, and inter-process flows of materials and energy	Cost and benefit monetary flows directly impacting decision maker
Units for tracking flows	Primarily mass and energy; occasionally volume, other physical units	Monetary units (e.g. dollars, euro.)
Time treatment and scope	The timing of processes and their release or consumption flows are traditionally ignored; impact assessment may address a fixed time window of impacts (e.g., 100-year time horizon for assessing global warming potentials) but future impacts are generally not discounted	Timing is critical. Present valuing (discounting) of costs and benefits. Specific time horizon scope is adopted, and any costs or benefits occurring outside that scope are ignored.

connected processes, resources and consumption flows. LCC assesses the cost-effectiveness of investments and business decisions from the perspective of an economic decision. Based on the merits and shortcomings of LCA and LCC, he described two approaches to combine them to get proper and full product or process design decision making, i.e., PTLaser and TCAce. PTLaser is the approach with traditional LCA process modeling capabilities and LCC capabilities. From the user inputs it can give LCA results (life cycle inventories for the modeled system alternatives), LCC results (financial evaluations of all alternatives), present valuing costs and benefits. TCAce is same as that presented by Constable, et al. (2000). He gave no results or applications of these methods.

Xie, et al. (2001) provided the theoretical model in the study on lifecycle and agility of process industry, which are different from TCA methodology. The enterprise agility is measured by four items, i.e. cost (C), time (T), robustness (R) and scope of change (S). The agility variables of process systems are: material flow variable (M), energy flow variable (E), information flow variable (I), humanware flow variable (H), cost flow variable (C) and workpiece flow variable (W). The four items C, T, R and S have the general function relationships without any specific information as following:

$$C = f_1 (M, E, I, H, C, W)$$

$$T = f_2 (M, E, I, H, C, W)$$

$$R = f_3 (M, E, I, H, C, W)$$

$$S = f_4 (M, E, I, H, C, W)$$

where f_1, f_2, f_3 and f_4 stand for functions (Xie, et al., 2001). The lifecycle mathematics model with agility variables of process systems would be used to determine agility degree and find out the key step or the "blunt point" responding to the change of process systems in different phases of whole lifecycle, in order to guide decision-making for an enterprise. They described agile manufacturing as a dynamic integration of enterprises from lifecycle, which requires incorporating flexible manufacturing systems and human resources to get maximum benefits in the long term. They set the target of agile manufacturing as global optimization of social, economic, resources and environment. However, they only gave the brief introduction about lifecycle and agile manufacturing which is developing without any specific example.

In summary, TCA is the important tool that can be used in chemical complex optimization. The key point is how to get the accurate assessment of the total costs for processes. Generally, industrial companies have the similar methods to calculate the first four type costs (Type I to Type IV) and have more experiences in considering former two costs than latter two costs. Hence the Type V cost, i.e. sustainable cost (external cost), will be reviewed next in detail. As the environment deteriorates and the global temperature rises, more and more people are concerned about the sustainable development of industries. Therefore, the sustainable cost associated with sustainable development, which was not considered in the past, is now being taken into consideration.

C. Sustainable Development and Sustainable Cost

Geiser (2001) stated the needs to design less toxic materials and processes that use materials without wastefully dissipating them, i.e. sustainable development with respect to materials. He put forward two strategies to support sustainable materials economy. One is detoxification of materials used in products and industrial processes. The other is development of ways to use less material to satisfy the same human needs, a process known as dematerialization. Six principles for a sustainable materials economy are listed as: closing the loop on material flows; increasing the intensity of material use; substituting services for products; reducing the dissipation of degradable toxic materials; reducing the use of persistent, bio-accumulative and toxic materials; developing more environmentally appropriate materials.

Daly (1990) gave the operating principles for sustainable development as follows. For renewable resources, the sustainable rate of use should be no greater than the rate of regeneration. For nonrenewable resources, the sustainable rate of use should be no greater than the rate at which a renewable resource being used sustainably can be substituted for it. For pollutant, the sustainable rate of emissions should be no greater than the rate of being recycled, assimilated, or degraded in the environment.

C-1. Sustainability

Graedel and Klee (2002) stated that sustainability could become a program capable of implementation only with numerical goals and targets. Ultimate sustainability and truly equitable environmental policy will only be achieved by balancing economic, environmental, and equity concerns. They gave the things to sustain, which are holocene-style climate (thermal balance, ocean currents, etc.); functioning planetary ecological systems (wetlands, forests, etc.); stocks of resources; earth’s organisms; and political and economic stability with tolerable variations. They listed several examples to demonstrate the complexity of sustainability. They also addressed some contentious issues, such as the weight factors for different sources, dynamic change of resource, sustainable use rate, and maintaining resources availability while maintaining living standards.

In summary, sustainability is about making choices and rendering actions that leave no unnecessary environmental strain for future generations. Sustainability calls for balancing the economic concerns with the environmental and social issues (Graedel and Klee, 2002).

C-2. Sustainability Measurement

Different ways and methods to measure sustainability will be discussed in the following sections. These include sustainability metrics, index, indicator and cost, along with uncertainty assessment. In addition, some examples will be presented.

C-2-1. Index for Measuring Sustainable Development

Since sustainable development calls for the balance among the economic concern, and environmental and social issues. Krotscheck and Narodoslawsky (1996) proposed the Sustainable Process Index (SPI), which is a highly aggregated index that measures the total environmental impact of human activities of various kinds. They combined the three criteria of sustainable development with the following requirements: material flow not exceeding assimilation capacity, being smaller than natural fluctuations in geogenic flows, not altering the quality and quantity of global material cycles; and natural variety of species and landscapes must be sustained and improved. The emphasis of SPI lies in embedding a process into ecological systems rather than in accounting their impacts on the environment (Figure 2.1). The concept of the SPI is based on the assumption that in a truly sustainable society the basis of the economy is the sustainable flow of solar exergy, which is energy from sunlight that can be converted to work. The conversion of the solar exergy to service needs “area”.

Thus “area” becomes the limiting factor of a sustainable economy. “Area” is the size of the land to provide energy, materials and space.

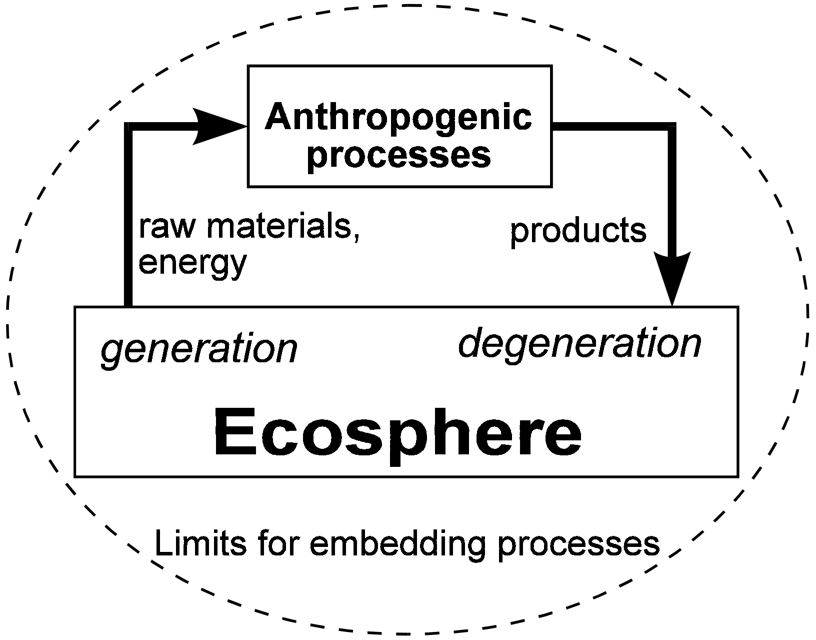


Figure 2.1 Ecosphere and Anthroposhere, from Krotscheck and Narodoslawsky (1996)

The SPI is the relation of two “areas” in a given time period (usually per year) for providing one inhabitant with a certain service or product. One “area” is needed to embed the process to produce the service or product unit sustainably into the ecosphere, a_{tot}, i.e. all things the process needs to run sustainably are stood by the “area”. The other is the “area” available (on a statistical base) for every inhabitant to guarantee its sustainable subsistence, a_{in}. The total area $\mathrm{A}_{\mathrm{tot}}$ is the sum of A_R, A_E, A_I, A_S and A_D as given by the following equation.

$$A_{tot} = A_R + A_E + A_I + A_s + A_D$$

$$a_{tot} = \frac{A_{tot}}{N_P}$$

$$SPI = \frac{a_{tot}}{a_{in}}$$

where A_R is the area for raw material production; A_E is the area for energy supply; A_I is the area for physical installation; A_S is the area to support the staff; A_D is the area for sustainable dissipation to ecosphere of products, all wastes and emissions; N_P is the number of goods or services produced by the process in question.

An example in Figure 2.2 shows the SPI of ethanol for use as fuel. In Europe one inhabitant can have 9320 kWh of primary energy from liquid fuel. The SPI of ethanol is 1.07×10^{-4} cap/kWh, which stands for the fraction of the area per inhabitant used for 1 kWh of primary energy supplied by liquid fuel. The smaller is SPI, the better it is. Based on the contribution of each partial area in the SPI, possibilities of reducing the SPI are recycling of materials, using energy and material cascades and multiple uses of areas. They gave general rules for process design regarding switching to renewable raw materials, recycling non-renewable materials, switching from fossil to renewable energy sources and adapting locally. These rules give specific information on how to reduce the SPI value.

Figure 2.3 shows the interface and principles to use SPI. The block “SPI calculation” represents the syntax of transforming process data into the partial areas, which is done with the help of the “SPI data resource”. There are three data banks in SPI data resource, i.e. regional data bank, process data bank and scenario data bank.

The regional data bank includes specific yields for already calculated products, yields for renewable resources and energy, energy data of installations, relation factors for the retropagatoric method, area feedback factors and data concerning rate of renewal and concentration of substances of the environmental compartments. Already-calculated processes are stored on an aggregated information level in the process data bank. On one hand this aggregation regards the partial areas and on the other hand a user-defined classification is possible. The results of one simulation are called a scenario and are stored in scenario data bank. A scenario in the SPI analyses consists of the partial areas and the SPI itself. These scenarios can be stored and compared. The analysis of scenarios visualizes different process alternatives or simulation states and help people to check for bottle-necks or best processing methods. The analysis can be stored in a scenario data bank.

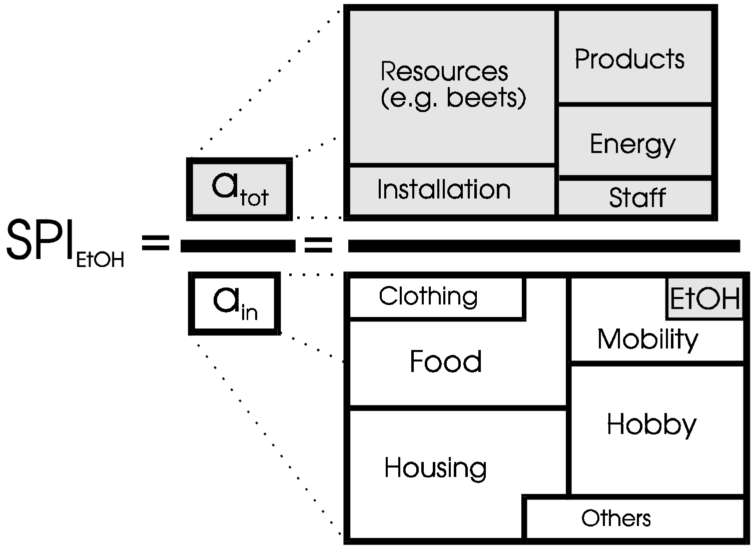


Figure 2.2 SPI of Ethanol for Use as Fuel, from Krotscheck and Narodoslawsky (1996)

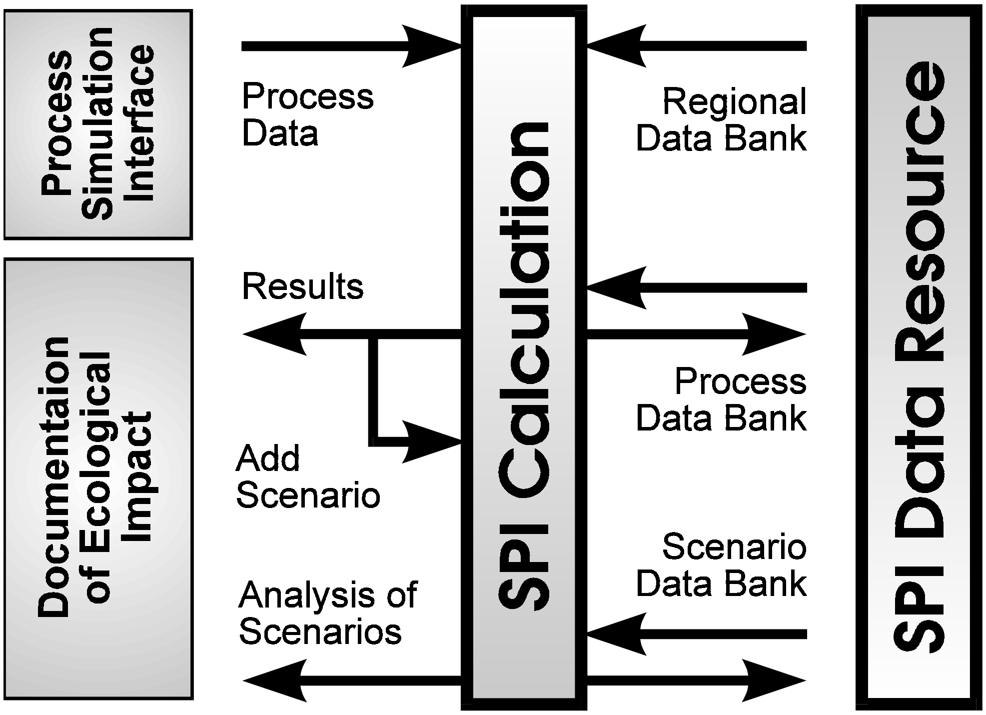


Figure 2.3 Interface and Principle of the SPI Routine, from Krotscheck and Narodoslawsky (1996)

Narodoslawsky and Krotscheck (2001) also proposed the SPI as an ecological evaluation system for the requirement of process engineering with the comparison of different systems and the various partial pressures from one system on the environment. They employed the SPI in the case study of evaluation of different energy production systems. Firstly they compared specific total areas (a_{tot}) for the generation of 1 kWh electricity via different energy systems (Figure 2.4). From Figure 2.4 they concluded that energy systems based on fossil, for example natural gas, have a clear disadvantage compared to those on renewable energy systems; and there are substantial differences among renewable energy systems, such as hydro power with big advantage. Secondly they presented the SPI methodology for identifying partial pressures from each of those energy systems on the environment (Figure 2.5), where energy is grey energy that is the energy needed to produce the energy product, for example electricity. The conclusions from Figure 2.5 are as follows: the natural gas turbines give main pressure on the environment from the raw materials (the fossil energy carrier) which can not be reduced; the main pressure from photovaltaics is grey energy which can be lessened if the more environmental friendly energy systems for grey energy are available, which is same to the hydro power and biomass steam cycles; the impact of the dissipation of emissions from biomass steam cycles is large because high nitrogen content in the biomass fuel that shows up in the flue gas as NO_x emission, which can be alleviated by these emission reductions.

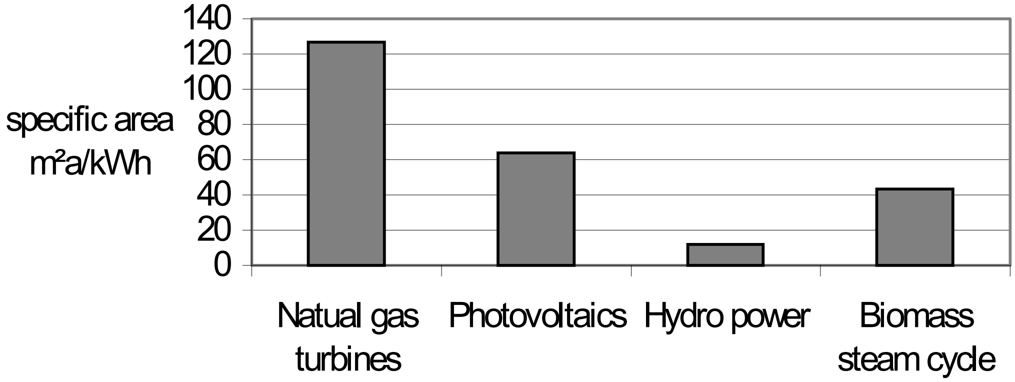


Figure 2.4 Specific Areas for the Generation of 1 kWh Electricity via Different Energy Systems, from Narodoslawsky and Krotscheck (2001)

In summary, SPI is an ecological evaluation system for industrial processes considering the environment as a significant factor in making decisions of future projects. SPI allows a clear rating of different technological pathways to provide goods or services. It has the strong capacity to compare different ecological impacts for a deeper analysis of the bottlenecks from the viewpoint of sustainable development for each different process, and pinpoint the important aspects of the environmental pressure of certain technology and guide the way for optimization and technological improvement.

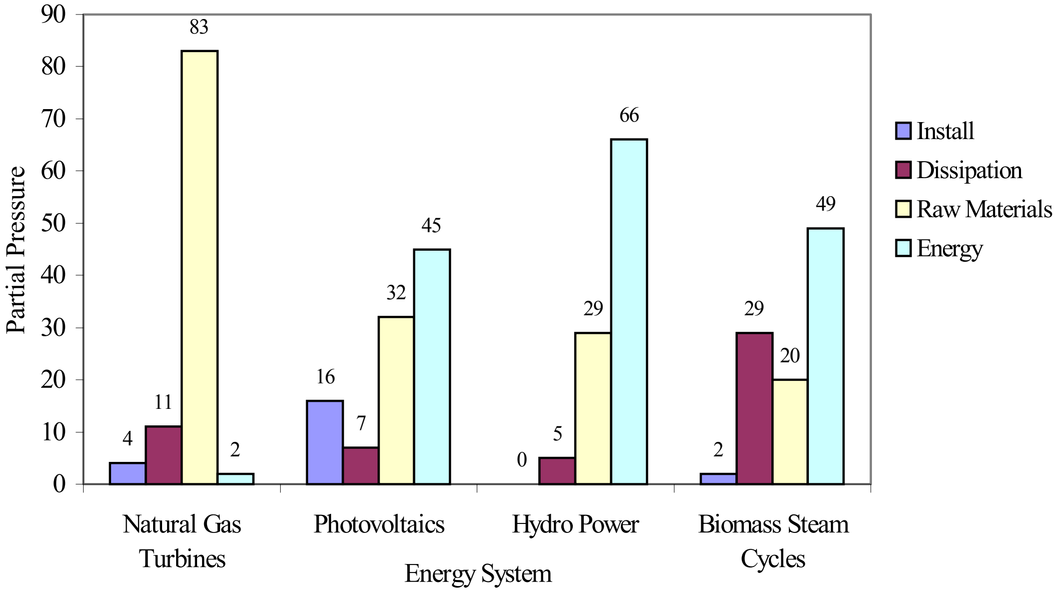


Figure 2.5 Analysis of Partial Pressure for Different Energy System, from Narodoslawsky and Krotscheck (2001)

Chen and Shonnard (2001) incorporated environmental and economic factors together. Their research was undertaken with the help of a commercial process simulator (HYSYS) and an integrated suite of process evaluation software tools (SCENE). The economic assessment uses economic indices that include Fixed Capital Investment (FCI), Net Present Value (NPV) and Payback Period (PP). The environmental indices were used to quantify global warming, ozone depletion, acid rain, smog formation, human-ingestion-route toxicity, human-inhalation-route toxicity, human-ingestion-route-carcinogenicity toxicity, human-inhalation-route-carcinogenicity toxicity and ecotoxicity (fish toxicity).

For the environmental assessment the evaluation step involves application of weighting factors to each environmental impact category based on their “distance to target”, where the target value is sufficiently low to assure adequate protection of human and ecosystem health. Then an environmental process composite index is found. Analytic hierarchy process is applied to construct a single objective function combing the three economic indices, FCI, NPV and PP, into a single economic one. This is combined with the process composite environmental impact index to get the optimal operating configuration. Qualitative weightings for three economic indices and for economic and environmental attributes are generated by pair-wise comparisons of them. The final weighting factors are 0.82 and 0.18 for economics and environment, respectively and 0.11, 0.674, 0.216 for FCI, NPV and PP, respectively. This integrated assessment and optimization can be used to simultaneously assess the impacts of process design on the environment, process safety and bottom-line profitability, then enable better-informed solution to process design problems.

Together with this method Kemppainen and Shonnard (2002) also introduced two other methods, i.e., the Greenhouse Gases, Regulated Emissions, and Energy use in Transportation (GREET) and the Economic Input Output-Life Cycle Assessment (EIOLCA). They applied these three methods to determine the amount of environmental benefits for biomass to ethanol production from different regional feedstocks. They concluded that these three methods had different basis of calculation, scope and indices measured. Especially, they compared the EIOLCA and GREET methods: the EIOLCA method reported the emission transactions between industry sectors without taking into account vehicle operation; the GREET method accounted for the production, transportation and use of the ethanol fuel without considering the additional environmental impacts from industrial transactions.

C-2-2. Metrics and Indicators for Measuring Sustainable Development

Metrics for sustainable development should represent energy efficiency, material efficiency, recycling and recycle content capability, and toxic dispersion corrected for quantified toxicity and for exposure pathway, as described by National Academy of Engineering (NAE) (1999). They defined industrial environmental performance metrics, which are the basis of sustainability metrics, for the manufacturing and the product use (Table 2-4) along with specific metrics in chemical manufacturing (Figure 2.6).

Industrial environmental performance metrics are used to assess the environmental aspects of companies' operations, including operational metrics, management metrics and environmental condition metrics. Operational metrics measure potential environmental burden in term of inputs and outputs of materials and energy, such as quantity of materials (waste or energy) used per unit of product. Management metrics describe the information on steps being taken to influence operations, such as number of achieved objectives and targets, and number of costs attributable to fines and penalties. Environmental condition metrics give information on the health of the environment and how it is changing, such as concentration of a specific contaminant in ambient air at selected monitoring locations.

Table 2-4 Environmental Performance Metrics in the Chemical Manufacturing and for Chemical Product Use, from NAE (1999)

Manufacturing	Product Use
Resource Related	
Material intensity • Percent first-pass yield • Percent ultimate yield • Percent process uptime • Percent atomic efficiency • Percent postconsumer waste used • Material efficiency (unit consumptions, including water/pound of product)	Material intensity[a] • Value per pound • Pounds replaced • Resources saved
Energy intensity • BTUs/pound • Total energy use • Minimum "practical" energy use	Energy intensity[a] • Value/BTU used • Energy saved by use
Packing • Total pounds • Pounds/pounds of product	Renewable • Percent of product • Recyclable
Environmental-Burden Related	
Environmental incidents • Frequency • Severity • Practical worst-case scenario	Packing • Recyclable • Biodegradable
Toxic dispersion • Airborne toxics • Carcinogens • Volatile organics • Particulates • Acid gases • "Hazardous" wastes • Aquatic toxicity/oxygen demand • Listed hazardous air (and water) pollutants • TRI chemicals (EPCRA Title III Section 313) • 33/50 chemicals	Toxic dispersion • Global warming • Ozone depletion • Persistence • Bioaccumulative • Hormone mimics
Product stewardship • Responsible Care • Environmental audits	Product stewardship • Responsible Care
Illnesses and injuries • Illness frequency and injury frequency • Employee "wellness"	Product stewardship • Use warning • User training

Table 2-4 (Continued)

Manufacturing	Product Use
Hazardous materials handling • Worker training	

a. Most product-use related material and energy intensity metrics deal with the product itself (e.g., value or energy use per pound). These metrics fail to capture the savings in energy or materials that may accrue from the use of the product.

Note: Italics indicate terms for which there are no agree-upon definitions. Potential metrics in these areas will depend on developing common definitions and agreement on their scientific underpinnings.

Since sustainability concerns ecological, economic development, and societal equity, those indicators directly affect these three concerns and are called 3-D (Sikdar, 2003). 1-D and 2-D indicators can be identified similarly. Hence, there are three groups of indicators (Figure 2.7). Group 1 (1-D) includes economic, ecological, and sociological indicators. Group 2 (2-D) includes socio-economic, eco-efficiency, and socio-ecological indicators. Group 3 (3-D) includes sustainability indicators. The hierarchical metrics scheme can systematize the sustainability analysis of products, processes and business enterprises. The hierarchical scheme for sustainable process is a multiobjective optimization (Sikdar, 2003). The cost of manufacture is first minimized while improving all 3-D indicators. Then, 2-D and 1-D indicators are to be examined while 3-D ones go the right way.

Based on the different purposes to compare companies across all industry sectors, within peer group and for internal managing, Arthur D Little (2000) showed that a balanced mix of leading and lagging, quantitative and qualitative, financial and non-financial indicators should be chosen. Leading indicators are used to anticipate future results, while lagging indicators are measured after the event.

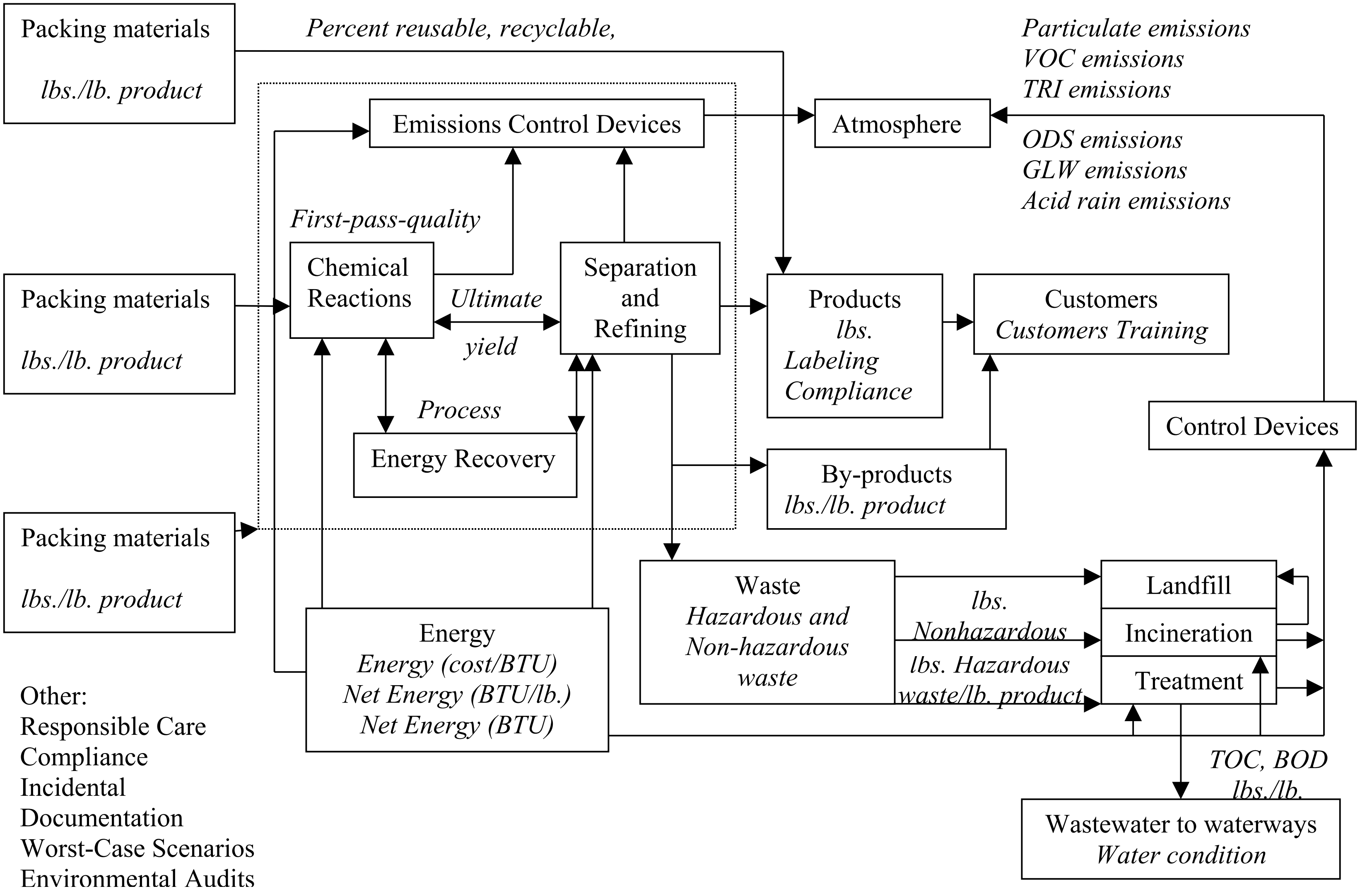


Figure 2.6 Metrics Used in Chemical Manufacturing, from National Academy of Engineering (1999)

Note: VOC—volatile organic compound; TRI—toxic release inventory; ODS—ozone depleting substances; GLW—Great Lakes waste; TOC—total organic carbon; BOD—biological oxygen demand

For example, R & D investment is a leading indicator of new product introduction, and the increased sale is a lagging indicator. So leading indicators are more likely to be of interest to stakeholders while lagging indicators are more amenable to independent verification. In addition, Arthur D Little (2000) also gave another indicator types: input, output, outcome, and process indicators. Input indicators represent things directly under the company control, which is measured in financial or other resources allocated to a particular end. Output indicators stand for the direct result of that resource allocation and outcome indicators are for the ultimate goal to which the relevant processes are directed. Process indicators are the back-up of the first three indicators.

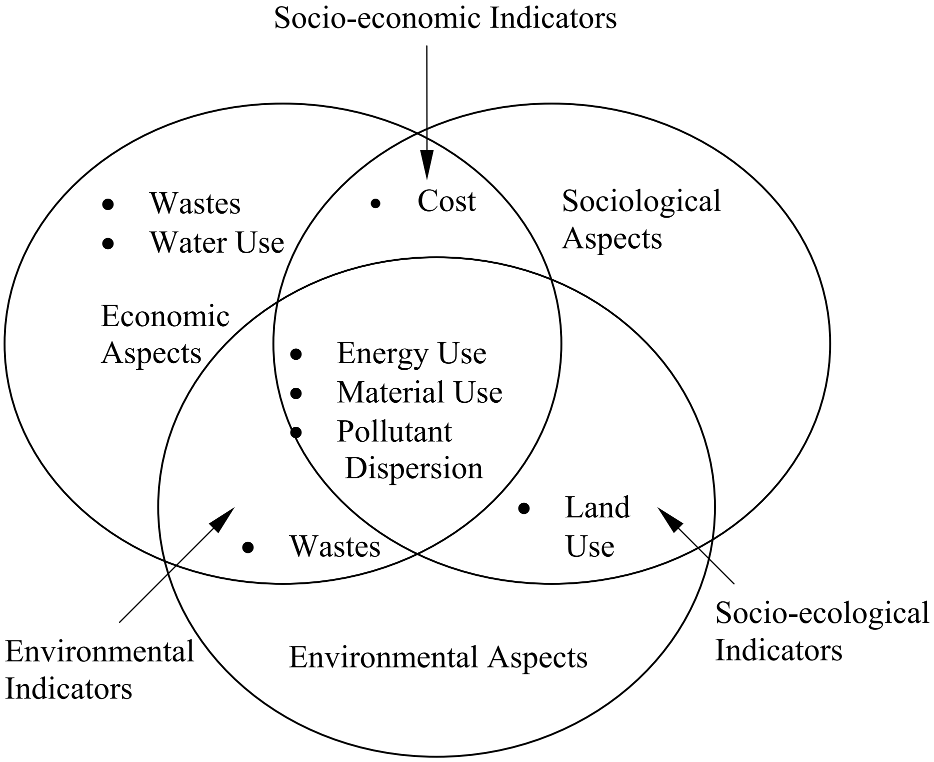


Figure 2.7 Hierarchical Sustainable Metrics System, from Sikdar (2003)

Carberry and Beaver (2000) developed baseline metrics whose qualities are presented in Table 2-5 for sustainable development in their collaborative projects. Their initial focus is that eco-efficiency metrics should cover material intensity, energy intensity, toxics dispersion, material recyclability, use of renewable resources, product durability and service intensity. For example, mass intensity metrics is equal to total mass in (raw materials, products, packaging) divided by value added (VA), where VA is the difference between total value of lbs. Product sold and purchase cost of raw material, packaging and energy. Energy intensity metric is equal to total BTU's conversion energy consumed divided by value added. They also gave some sustainability metrics values from Industrial Assessment Center (IAC) database. For instance, for sulfuric acid produced from sulfur material intensity metrics is 16.8 lb/$VA and energy intensity metrics is -4.87 KBTU/$VA. For phosphoric acid produced from the wet process the material intensity metrics is 171.3 lb/$VA and energy intensity metrics is 176.2 KBTU/$VA.

Table 2-5 Qualities of Successful Metrics, from Carberry and Beaver (2000)

Quality	Definition
Efficient	1. Few, robust and non-perverse; 2. Simple to collect, calculate, understand and reproduce; 3. Based on available data
Business and environmental value	1. Providing for growth of business value, standard of living; 2. Relevant to the business involved (useful management tool); 3. Related to economic criteria; promotes the right behavior; 4. Driving and documenting continual improvement of value to the general public; 5. Improving international environmental quality.
Ideal	A core set of metrics universally accepted with additional metrics specific to each business or operation
Normalizable	Sustainability metrics normalization is important for analysis, prioritization and comparison.

BRIDGES to Sustainability (2002) described sustainability metrics as consolidating key measures of environmental, economic and social performance. They defined five basic metrics and six complementary metrics (Table 2-6). General characteristics of metrics are that the lower the metric, the better the process or product in terms of sustainability, and a metric can be negative when co-product energy or waste stream is a raw material. They gave the sustainability metrics of carpet tile in Table 2-7 and compared the metrics of different products (Table 2-8) and different processes for same product, for example, acetic acid (Table 2-9). They concluded that sustainability metrics can be improved by decreasing impact, increasing output or improving social performance.

Table 2-6 Sustainability Metrics, from BRIDGES to Sustainability (2002)

Basic metrics	Complementary metrics
1. Materials $\frac{\text{Mass of raw materials-Mass of products}}{\text{Output}}$ 2. Water consumption $\frac{\text{Volume of fresh water used}}{\text{Output}}$ 3. Energy use $\frac{\text{Net energy used}}{\text{Output}}$ 4. Pollutant dispersion $\frac{\text{Total mass of pollutants released}}{\text{Output}}$ 5. Toxics dispersion $\frac{\text{Total mass of recognized toxics released}}{\text{Output}}$ Output is mass of product or sales revenue or value-added.	1. Greenhouse gases 2. Acidification 3. Eutrophication 4. Stratospheric ozone depletion 5. NO_x emissions 6. VOCs 7. Packaging 8. Recycled content 9. Rainwater

Table 2-7 Carpet Tile Sustainability Metrics, from BRIDGES to Sustainability (2002)

Metrics	Mass of product (/lb)	Sales revenue (/$)	Value-added (/$)
Material (lbs)	0.042	0.021	0.035
Energy (KBTU)	1.27	0.65	1.07
Water (gal)	0.14	0.079	0.13
Toxics (lbs)	0.0	0.0	0.0
Pollutants (lbs)	0.66	0.34	0.55

Table 2-8 Sustainability Metrics for Different Products Based on Value-Added, from BRIDGES to Sustainability (2002)

Metrics	Acrylonitrile from propylene	Adipic acid from cyclohexane	Phosphoric acid from dihydrate wet process
Material intensity (lbs/$)	4.68	1.04	318
Water consumption (gal/$)	32.0	8.94	208
Energy intensity (KBTU/$)	49.5	27.7	195
Toxics dispersion (lbs/$)	0.14	0.0002	4.22
Pollutant dispersion (lbs/$)	0.291	0.0174	0.00

Table 2-9 Sustainability Metrics for Different Processes Based on Value-Added, from BRIDGES to Sustainability (2002)

Metrics	Acetic acid from low pressure process	Acetic acid & acetic anhydride from BP Chemicals	Acetic acid & acetic anhydride from Eastman process
Material intensity (lbs/$)	0.39	0.76	0.73
Water consumption (gal/$)	7.88	5.19	2.23
Energy intensity (KBTU/$)	11.6	13.9	4.83
Toxics dispersion (lbs/$)	0.0007	0.00006	0.00001
Pollutant dispersion (lbs/$)	0.00	0.00	0.016

Tanzil, et al. (2002) described applications of the sustainability metrics. They considered the sustainability metrics as decision-support tools in evaluating different strategies and technologies, and in comparing different facilities and measuring progress towards sustainability. Sustainability metrics can be used to identify successive levels of improvements in energy efficiency of chemical manufacturing processes. Meanwhile, the environmental impacts from the changes in energy consumption can be evaluated with the sustainability metrics. This work was extended to the application of sustainability metrics to two maleic anhydride processes, to toolbox manufacturing facilities and to design of steel components (Tanzil and Beloff, 2004).

Fiksel, et al. (1998) gave the three principles of a sustainability performance measurement framework: separation of resource and value measures, explicit representation of the triple bottom line, and consideration of the full life cycle. Built upon those three principles, a Sustainability Performance Measurement (SPM) framework for products, processes or services can be designed. Thus, the sustainability of a product can be evaluated with this framework. They also stated appropriate performance indicators and accompanying metrics can best stand for the contribution of the product to sustainability and should be selected once a SPM framework has been established. They defined a performance indicator as a specific measurable product attribute that characterises its contribution to some aspect of sustainability. The performance indicator must be associated at least one metric that defines a specific means of tracking and reporting that indicator. They described two categories of performance indicators, i.e. lagging and leading, and two broad categories of metrics, i.e. quantitative and qualitative (Table 2-10). Quantitative metrics relies on empirical data and characteristics performance numerically, e.g. dollars of revenue. Qualitative metrics relies upon semantic distinctions based on observation and judgement. Selecting indicators and metrics should be based on mixed approach, that is quantitative indicators are used when the measurement data can be obtained cost effectively, then qualitative indicators for other critical aspects of sustainability can be employed. They gave a biotechnology product example that is new pest-resistant crops to show how to select indicators and metrics (Table 2-11).

Table 2-10 Examples of Indicators and Metrics, from Fiksel, et al. (1998)

	Quantitative metrics	Qualitative metrics
Leading indicator	Sustainability training (number of employees trained)	Sustainability training (employees evaluation of training courses)
Lagging indicator	Product eco-efficiency (lbs. product/total lbs. input)	Product eco-efficiency (stakeholder satisfaction or number of awards)

Table 2-11 Sustainability Indicators for a Biotech Agricultural Product, from Fiksel, et al. (1998)

Indicators	Supply	Manufacturing	Use	Distribution
Economic		Economic value added	Farmer productivity (bushels/year)	Food costs ($/bushel)
Environmental	Material intensity (lbs/year)	Toxic emissions (lbs/year)	Genetic transference risk (qualitative) Pesticide use (gal/bushel) Fuel consumption (gal/bushel)	
Societal		Employee injuries (number/year)		Public health risk (qualitative)

Kheawhom and Hirao (2001) studied the decision support tools, which are capable of reducing the complexity of the process synthesis problem and analyzing a trade-off between the environmental impact, economy and robustness of the process with economic, environmental and process robustness indicators. The economic indicator is product revenue minus the summation of fixed costs and operating costs. The environmental indicator is SPI (Krotscheck and Narodoslawsky, 1996). The process robustness indicator is represented by process controllability and operability. Process controllability is indicated by the failure probability that is defined as the probability of failure scenarios. The process operability is evaluated by the deviation ratio to investigate how cost or environmental impact increases when a fluctuation of input occurs. The method is to construct the multi-criteria optima surface (MOS) which is a surface obtained from a plot between objective functions and other criteria, and this surface shows how each criterion changes under given circumstances. He also gave a closed-loop volatile organic compound (VOC) recovery process as an example in the case study where the MOS plot analysis between the three indicators are employed and the environmentally benign process is selected. Even though the methodology is only for the single process, it is capable of designing and selecting the process flowsheet with minimal environmental impact and maximal robustness at a desired economic performance.

BRIDGES to Sustainability (2002), Tanzil, et al. (2002) and Schwarz, et al. (2001) used the energy consumed per unit of output as a key indicator of the sustainability for a manufacturing process to determine the Practical Minimum Energy (PME) requirements. There are five levels of energy requirements using data from the Process Economic Program Library (PEP) at SRI International. The levels from Level 0 to Level 4 are base case, PEP-benchmark case, optimum heat integration, process redesign and theoretical energy requirement, respectively. The evaluation of these five cases mostly depends on the comparison of net fuel energy consumed by process, total energy consumed by process and total energy consumed by product chains. The net fuel consumed by process is the net fuel energy consumed to provide heat and power for the process excluding the energy contained in the raw materials. The total energy consumed by process is the sum of net fuel energy and the raw material energy consumed by the process, where the raw material energy is the difference in enthalpy between the raw materials and the products. The total energy consumed by product chain is the sum of total energy consumed by process and that consumed in the productions of the raw materials, which is used to compare processing options involving alternative raw materials. Tanzil, et al. (2002) gave the PME levels of maleic anhydride production via the oxidation of n-butane as an example (Table 2-12), where Level 3 is the most efficient in terms of total energy consumed by process. Meanwhile, BRIDES to Sustainability (2002) illustrated the PME level results of different products (Table 2-13). This methodology is a valuable tool in decision-making for chemical producers, and helps managers to assess current performance, set goals for improving energy efficiency, and include the concept of sustainability in long terms of objectives for business and environmental performance.

C-2-3. Cost and Uncertainty for Measuring Sustainable Development

Koomey and Krause (1996) gave an introduction to externality costs, which is synonymous with sustainable cost. Externality is defined as social costs that are not reflected in market transactions, and now it is especially used in energy plants. When externality costs are analyzed there are four steps, i.e. insults to physical and human environment, pathways (convert insults to stresses), stresses (physical or social consequences of insults), and environmental and social costs of insults. The externality formula is as follows:

Externality Cost = Size of Insult × Value of Environmental Damage

Table 2-12 PME Levels for Production of Maleic Anhydride via the Oxidation of n-Butane, from Tanzil, et al. (2002)

Energy requirement (BTU/lb-product)	Level 0	Level 1	Level 2	Level 3	Level 4
Fuel energy required for electricity generation	4,581	4,581	4,581	4,097	
Fuel energy required for steam generation	5,036	2,249	1,574	2,711	
Auxiliary fuel required for incineration	3,227	3,227	3,227	252*	
Total fuel energy required	12,844	10,057	9,382	7,060	
Fuel energy credit	-12,077	-12,077	-12,077	-19,483	
Net fuel energy consumed by process	767	-2,020	-2,695	-12,423	-5,522
Raw material energy consumed by process	15,025	15,025	15,025	19,812	5,522
Total energy consumed by process	15,792	13,005	12,330	7,389	0

*Auxiliary fuel is added to the waste stream for the generation of additional steam in Level 3 process.

Table 2-13 Total Energy Consumed by Process for Different Products in PME, from BRIDGES to Sustainability (2002)

BTU/lb-product % reduction from Level 0	Level 0	Level 1	Level 2	Level 3
Acetic acid	3,625 0%	3,625 0%	3,584 1%	3,293 9%
Acetic anhydride	2,785 0%	2,770 1%	2,450 12%	2,217 20%
Maleic anhydride	15,792 0%	13,005 18%	12,330 22%	7,389 53%
Terephthalic acid	11,319 0%	10,038 11%	10,038 11%	7,818 31%
Caprolactam	35,805 0%	35,805 0%	33,184 7%	23,501 34%

where Externality Cost is the total external cost to society, in dollars; Size of Insult is expressed in physical units (lbs emitted or hectares degraded); Value of Environmental Damage (VED) is expressed in dollars per physical unit of insult. The estimates of externality costs vary as a function of population density, geographic and meteorological conditions, stringency of emissions regulations, and other factors. Externality costs must be normalized to some common unit of service for consistent comparison. Consistent comparisons require those environmental insults from both energy efficiency and supply technologies must be included in externality assessments. They presented the methods of calculating the value of emissions reductions, which are direct damage estimation and cost of abatement. The latter one is also called revealed preferences. Usually control of abatement yields higher externality values than do direct damage estimation. For example, the externality costs for NO_x in air basin of San Diego from direct damage estimation and cost of abatement are \$2.78/lb and \$9.15/lb in 1989, respectively. The externality cost of CO_2 based on direct damage estimation in 1989 from Pace University is \$0.026/lb-C, and from Minnesota the range is \$0.09/lb-C to \$0.021/lb-C. Even though there are large uncertainties in assessing externality costs, the externality cost should be incorporated in the analysis of the triple bottom line.

In power generation systems, externality costs, namely the electricity externality costs, have been studied for over ten years. In Table 2-14 some of these types of costs are presented by Rowe, et al. (1995). These costs have different names, such as carbon taxes, and different values. There are carbon taxes on fossil fuels, such as about \$1.5 per ton of CO_2 in Finland and over \$45 per ton of CO_2 in Sweden.

Table 2-14 Selected Carbon Dioxide Values (\$/Short Ton of CO_2 in 1992), from Rowe, et al. (1995)

State or Program	\$/Short Ton of CO_2
Forest management (Coastal Environmental Services, 1992)	1 to 5.50
New York (NY PSC Order 89-15)	1.2
Massachusetts (MA DPU Orders 89-239/91-131)	25
Wisconsin (PSC Order, Docket No. 05-EP)	15
California 1992 Electricity Report	8.7
DICE Model (Nordhaus (2))	1.4
New York State Draft 1994 Energy Plan	Low 3.1, Medium 6.2, High 12.4
Nevada (PSC Docket 89-752)	23
Oregon (Order 93-695)	10 to 40

Note: The low, medium, and high values are specified as a three-point discrete probability distribution from a beta distribution, which is unimodal and sufficiently flexible to allow symmetry or skewness in the distribution of values.

The environmental values, which are used in the economic model as the emission penalties, adopted by the Minnesota Public Utilities Commission are listed in Table 2-15. The table shows zero values for SO_2 starting after the year 2000 and shows zero values for CO_2 beyond the borders of the State of Minnesota. The SO_2 value is zero because SO_2 damages will be internalized after 2000 and, therefore, applying environmental costs would be double accounting.

Mann (2001) described cultural changes and water-asset realignment to support water-reuse projects when most people focused on toxics and carbon dioxide. He mentioned Water System Optimization (WSO) and the traditional costs associated with water use and discharge (Table 2-16). Industrial water reuse is recognized as a significant step towards reducing the impact of the chemical process industries on our

Table 2-15 Environmental Values for Emissions from Different Sites, from Sustainable Minnesota (2003)

	Urban	Metropolitan Fringe	Rural	Within 200 Miles of Minnesota
SO_2 (1995 to year 2000-$/ton)	112-189	46-110	10-25	10-25
SO_2 (after year 2000-$/ton)	0	0	0	0
PM10 ($/ton)	5,060-7,284	2,253-3,273	637-970	637-970
CO ($/ton)	1.20-2.57	0.86-1.52	0.24-0.46	0.24-0.46
NO_X ($/ton)	421-1,109	159-302	20-116	20-116
Pb ($/ton)	3,551-4,394	1,873-2,262	456-508	456-508
CO_2 ($/ton)	0.34-3.52	0.34-3.52	0.34-3.52	0

Table 2-16 Traditional Manufacturing Costs Associated with Water Operation, from Mann (2001)

Water Operation	Associated Costs
Intake	Water tariffs, solid disposal, pumping, maintenance
Treatment	Treatment chemicals, solid disposal, pumping, maintenance, capacity increases
Water Use	Pumping, maintenance, heating/cooling
Wastewater Treatment	Treatment chemicals, aeration, pumping, maintenance, heating/cooling, capacity increase
Discharge	Compliance monitoring, discharge tariffs, solid disposal, pumping, maintenance

environment. Thus, tools such as water-pinch technology, mass-exchange networks and mathematical optimization were a focus of process integration research during the 1990s. These tools are now available through commercial software packages and some focus has shifted towards implementation. Dow Chemical Company is leveraging the lessons learned in the integration of wastewater-treatment assets to the execution of projects to identify and implement water-reuse opportunities. Their first step was realigning freshwater-treatment assets under the control of a single global business unit. This approach provides an environment for accurately evaluating the true cost of water use and discharge and of managing water resources to ensure future freshwater supplies.

Montgomery and Needelman (1997) studied the welfare effects of toxic contamination in freshwater fish and estimated the benefits of removing toxic contamination from New York State water bodies. They linked the Environmental Protection Agency's Aquatic Based Recreation Survey with water-quality data from the New York Department of Environmental Conservation. Using a repeated discrete choice model of fishing behavior of fishermen, the elimination of toxic contamination from New York lakes and ponds would generate an annual benefit of about $63 per capita, per season. Their data permit estimation of welfare gains from eliminating acidity ($14.85 per capita per season), and other benefits listed in Table 2-17.

Table 2-17 Welfare Cost of Water Quality Problems, from Montgomery and Needelman (1997)

Problem	Compensating Variation		
	Per Trip	Per Capita per	
		Day	Season
Toxic Contamination	$1.51	$0.45	$63.25
Toxic Site Close to Fishing	$2.08	$0.62	$87.09
Acidity (threatened or impaired)	$0.32	$0.10	$13.82
Acidic Sites Closed to Fishing	$0.34	$0.10	$14.85
Toxic Contamination plus Acidity	$1.89	$0.56	$79.44

Shonnard, et al. (2001) considered the uncertainty analysis for toxicity assessment of chemical process designs. In any system, there are four categories of uncertainty for predicting environmental impacts, i.e., model-inherent uncertainty in both the process model and the environmental fate and transport model, process inherent uncertainty, external uncertainty, and discrete uncertainty. The uncertainty characteristics of the environmental properties from statistical analysis are propagated through the environmental impact assessment model including emission estimation, environmental fate and transport modeling, and relative risk assessment. In the case study of VOC recovery, they obtained results for the standard error in the inhalation toxicity index to be between 23.1% and 31.4% of the index's mean value. They said that the level of uncertainty could be predicted and used by process designers and decision-makers to discriminate between operating conditions that are statistically significant.

In summary, there are many ways to measure the sustainability and each has merits and deficiencies. Sustainability metrics and SPI are two important ones of them. Sustainable costs are required to be included with economic and environmental costs.

C-3. Eco-Efficiency

Eco-efficiency is a similar idea to sustainable development. In 1992, the Business Council for Sustainable Development (now the World Business Council for Sustainable Development) introduced the term "eco-efficiency". This term describes the extent to which corporations deliver competitively-priced goods and services that satisfy human needs and bring quality of life, while progressively reducing ecological impacts and resource intensity throughout the lifecycle to a level at least in line with the Earth's estimated carrying capacity.

Schwarz, et al. (2001) described the relationship between sustainability and eco-efficiency (Figure 2.8). Eco-efficiency is an important part of sustainability.

Accordingly, Beloff, et al. (2002) described an important subset of sustainability metrics, eco-efficiency metrics, which relate two of the three dimensions of sustainability, i.e. economic and environmental performance. Therefore, the appropriate metrics for social performance can be combined with the eco-efficiency metrics to simultaneously track progress in the sustainability areas, i.e. economic, environmental and social performance.

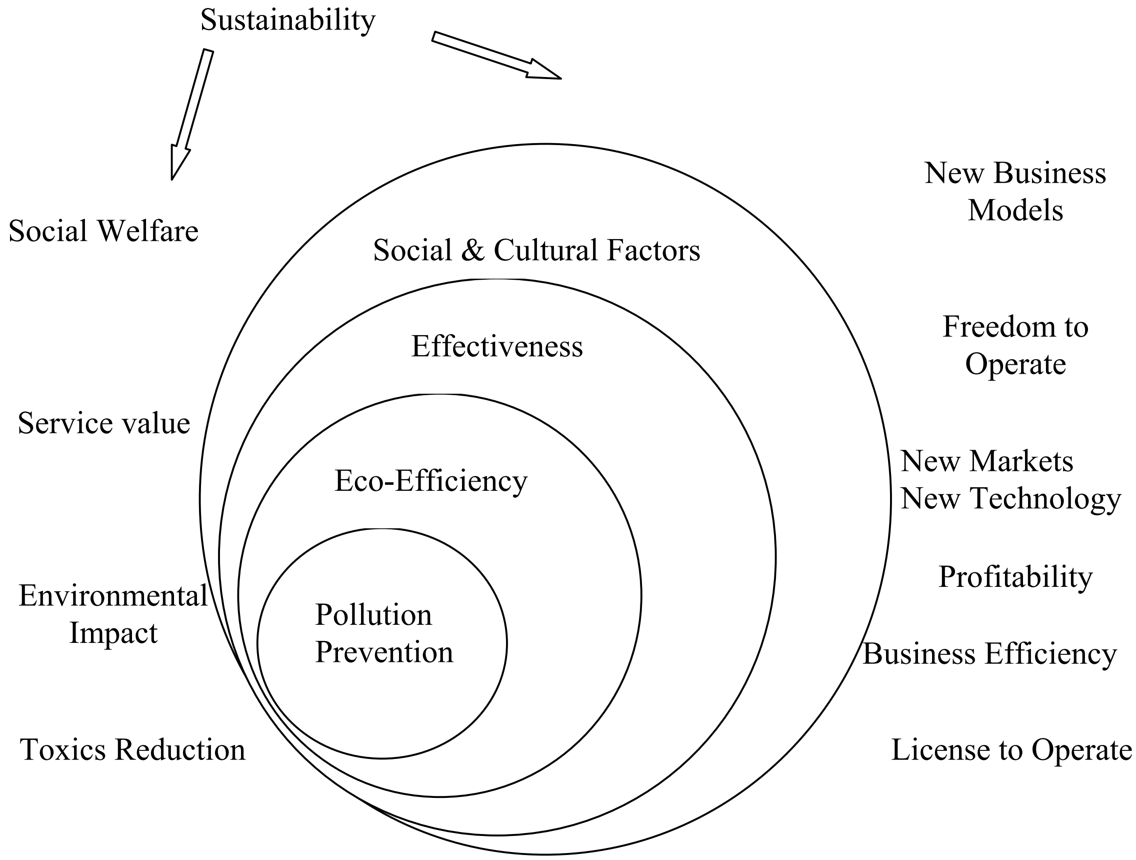


Figure 2.8 Eco-Efficiency vs. Sustainability, from Schwarz, et al. (2001)

Steinmetz (2001) provided the analytical tools to shape eco-efficient products and processes of the future. He used information on energy consumption, risk potential, materials consumption, emissions and toxicity to derive an "ecological fingerprint" over the entire lifecycles of the alternative processes for each product or service. The fingerprint is then combined with economic data to estimate eco-efficiency. He described the weighting factors for five categories of effects on the environment in Figure 2.9, where global warming potential plays a more important role than others in the atmosphere emissions. That is a reason why CO_2 reuse is reviewed later in this chapter. He concluded that eco-efficiency analysis can be used to compare and position products, and set product strategy.

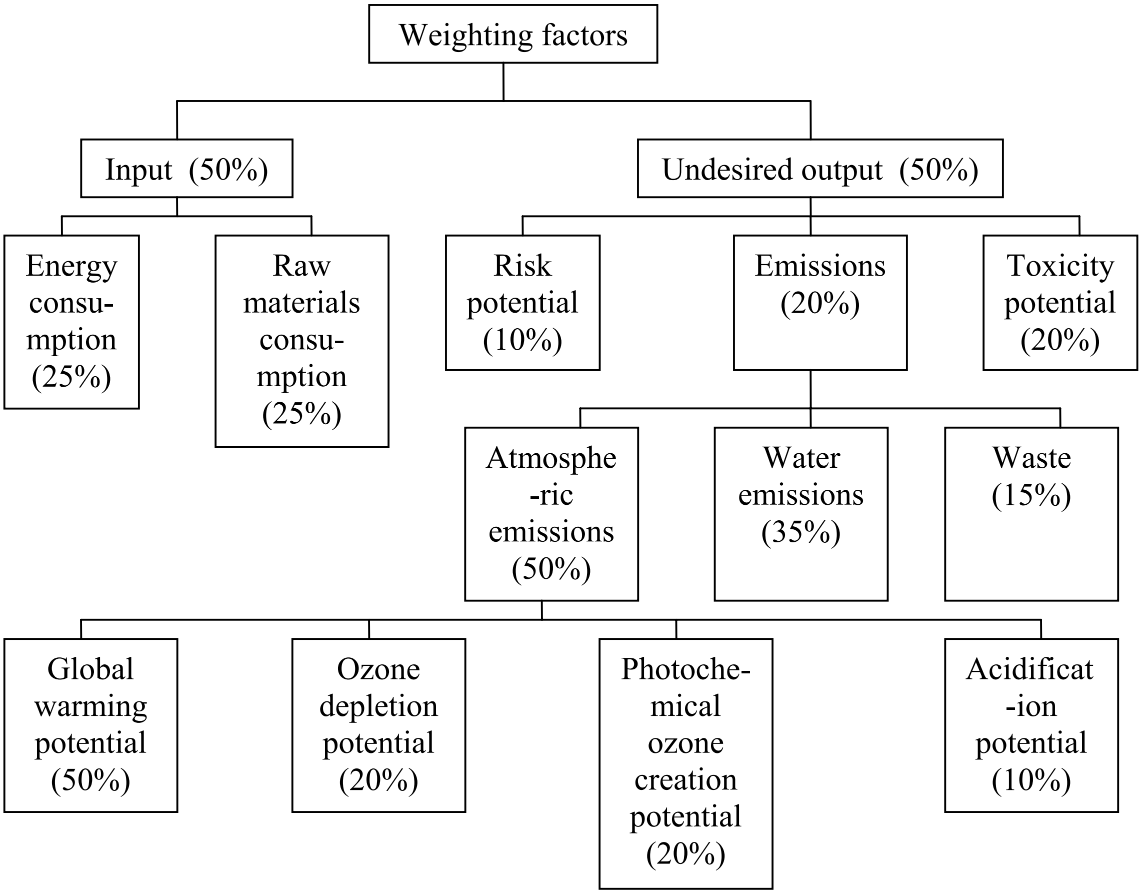


Figure 2.9 Weighting Factors of Effects on the Environment, from Steinmetz (2001)

Morse (1999) reported the status of eco-efficiency metrics that are employed by Dow, Dupont, ICI and Novartis companies, which tries to assess the economic and environmental impact of business operation with two types of indicators. Core indicators, such as greenhouse gas emissions, have relevance to all businesses. Supplemental indicators, such as the release of a particular toxic chemical, are highly dependent on a specific business. This approach is common for chemical producers to measure resource consumption, plant emissions, product value and recyclability. Also this focus on eco-efficiency excludes the social factors that need to be included.

In summary, eco-efficiency emphasizes the relationship between producing and ecology systems. Eco-efficiency is one part of sustainability, dealing with economic and environmental performance in the sustainability. Eco-efficiency metrics should be used together with social performance metrics to evaluate the sustainability of products or processes.

C-4. Green Chemistry and Green Engineering

As people pay more attention to the environment, green chemistry and green engineering have become more popular and are closely linked and coined. The Green Chemistry Program at EPA was launched by executive order to use chemistry for source reduction, the highest tier of the risk management hierarchy as described in the Pollution Prevention Act of 1990. The Green Engineering Program was established by EPA's Office of Pollution Prevention and Toxics to incorporate pollution prevention into process design. The program provides risk assessment screening tools to explore ways to minimize negative impact on human health and the environment. A textbook has been published on Green Engineering by Allen and Shonnard (2002).

Green chemistry, also known as sustainable chemistry, is an umbrella concept that has grown substantially since it became fully popular several years ago. Sustainable chemistry is defined by Organization for Economic Co-operation and Development (OECD) (1998) as

> "Within the broad framework of sustainable development, we should strive to maximize resource efficiency through activities such as energy and non-renewable resource conservation, risk minimization, pollution prevention, minimization of waste at all stages of a product life-cycle, and the development of products that are durable and can be re-used and recycled. Sustainable chemistry strives to accomplish these ends through the design, manufacture and use of efficient and effective, more environmentally benign chemical products and processes."

Ritter (2002) proposed that the aim of green chemistry was preventing pollution through better process design rather than by managing emissions and waste - the "end of pipe" solution. Green chemistry required all chemists and chemical engineers to use classical chemistry as well as emerging fields off biotechnology and nanotechnology to design chemical products and processes that have little or no impact on the environment. He also stated that the important areas of green chemistry included the use of renewable raw materials, direct oxidation using oxygen, improved separations technology, and all forms of catalysts.

Rodgers (2001) said that green chemistry involves designing chemical products and processes that reduce or eliminate the use and/or generation of hazardous substances. Also he stated that green chemistry involves a fundamental shift in the way that science views chemical design and synthesis.

Anastas, et al. (2001) gave the definition of green engineering, which is the design of systems and unit processes that obviate or reduce the need for the use of hazardous substances while minimizing energy usage and the generation of unwanted by-products. For example supercritical CO_2 is used in chemical processes in place of toxic solvents.

Anastas in CHEMRAWN XIV conference, which was cited in Ritter (2001), gave the reason green chemistry is being adopted so rapidly around the world is because it is a pathway to ensuring economic and environmental prosperity. He also said that the reason green chemistry is powerful is because it starts at the molecular level and ultimately delivers more environmentally benign products and processes.

Curzons, et al. (2001) proposed that long, medium and short-term paradigm for processes to be green is just like the pursuit of atom economy, the marriage of chemistry and engineering, and getting your house in order. They listed the categories of green metrics, i.e. mass, energy, pollutants or toxic dispersion, persistent and bioaccumulative, ecotoxicity, human health, photochemcial ozone creation potential, greenhouse gas emissions, safety and solvent. These metrics are similar with the chemical sustainability metrics, adding some metrics about solvents and for the single reactions not for the complex plant with more than one reaction. For example, the green metrics in mass are as follows:

$$\text{Mass intensity} = \frac{\text{total mass (kg)}}{\text{mass of product (kg)}}$$

$$\text{Reaction Mass Efficiency (RME)} = \frac{\text{mass of isolated product (kg)}}{\text{total mass of reactants used in reaction (kg)}} \times 100\%$$

$$\text{Atom economy} = \frac{\text{product molecule weight}}{\text{molecule weight sum of all reactants used in reaction}} \times 100\%$$

$$\text{Carbon efficiency} = \frac{\text{mass of carbon in product (kg)}}{\text{total mass of carbon in key reactants (kg)}} \times 100\%$$

The green metrics in energy are

$$\frac{\text{total process energy (MJ)}}{\text{mass of product (kg)}} \text{ and}$$

$$\frac{\text{total solvent recovery energy (MJ)}}{\text{mass of product (kg)}}.$$

The comparison of average atom economy with average reaction mass efficiency (RME) for some chemistries are listed in Table 2-18. They argued that RME is a more realistic metric to illustrate how far from "green" based on mass of the process, and mass and energy appear to be good leading indicators of overall environmental impact, although toxicity metrics are still evolving. Also in the short-term, rigorous management of solvent use is likely to result in the greatest improvements to making process greener. In addition, they gave a table of selected green metrics.

Table 2-18 Comparison of Average Atom Economy with Average RME for Five Chemistries, from Curzons, et al. (2001)

Chemistry type	Atom economy (%)	RME (%)
Resolution	40	31
Decarboxylation	77	68
Epoxidation	83	58
Sulfonation	89	69
Esterification	91	67

Tundo and Anastas (2000) dealt with the synthetic pathways and processes in green chemistry. They said that the development of new processes that are simultaneously economically sustainable and environmentally responsible is the challenge for the twenty-first century.

Anastas and Warner (1998) presented the tools for green chemistry to get its target as alternative feedstock (starting materials), reagents, solvents, product (target) molecule and catalysts, also process analytical chemistry to measure and control reaction conditions. They also listed the twelve principles of green chemistry as follows:

- prevent waste better than to treat or clean up waste after it is formed;
- design synthetic methods to maximize the incorporation of all materials used in the process into the final product;
- design synthetic methodologies to use and generate substances that possess little or no toxicity to human health and the environment;
- design chemical products to preserve efficacy of function while reducing toxicity;
- avoid auxiliary substances, such as solvents and separation agents, wherever possible and, innocuous when used;
- select raw material of feedstock to be renewable rather than depleting wherever technically and economically practicable;
- minimize environmental and economic impacts of energy requirements and try to conduct synthetic methods at ambient temperature and pressure;
- avoid unnecessary derivatization, such as blocking group, protection and deprotection whenever possible;

- catalytic reagents (as selective as possible) superior to stoichiometric reagents;
- design chemical products which do not persist in the environment and break down into innocuous degradation products at the end of their function;
- develop analytical methodologies to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances;
- choose substances and form of a substance used in a chemical process so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

Allen and Shonnard (2002) gave the detailed information about environmentally preferable or green approaches to the design and development of processes and products in their book Green Engineering. First they gave the characteristics of a chemical with low risk potential in aquatic environments and in the air listed in Table 2-19. They also studied the risk management, waste management, emission and waste modeling in the process design. The definition of risk is given by the Presidential/Congressional Commission on Risk Assessment and Risk Management (1997), which is the probability that a substance or situation will produce harm under specific conditions. Risk is a combination of two factors - the probability that an adverse event will occur and the consequences of the adverse event. Risk management is the process of identifying, evaluating, selecting, and implementing actions to reduce risk to human health and to ecosystems. The goal of risk management is scientifically sound, cost effective, integrated actions that reduce or prevent risks while taking into account social, cultural, ethical, political, and legal consideration.

Table 2-19 Low Risk Potential Chemical Characteristics in Different Medium, from Allen and Shonnard (2002)

Medium type	Low Risk potential chemical characteristics
In aquatic environments	1. High Henry's Law constant (substance will volatilize into the air rather than stay in the water) 2. High biodegradation (it will dissipate before exerting adverse health effects) 3. Low fish toxicity parameter (a high value of the concentration lethal to a majority of test organisms or LC_{50}) 4. Low Bio-Concentration Factor, BCF (low tendency for chemicals to partition into the fatty tissue of fish, leading to exposure and adverse health effects upon consumption by humans)
In the air	1. Low toxicity properties (high Reference Dose [RfD] for inhalation toxicity to humans or a low cancer potency) 2. Low reactivity for smog formation (ground level ozone production)

Allen and Shonnard (2002) defined chemical risk as a function of hazard and exposure:

$$\text{Risk} = f\,(\text{Hazard, Exposure})$$

Hazard is the potential for a substance or situation to cause harm or to create adverse impacts on persons or the environment. The magnitude of the hazard reflects the potential adverse consequences, including mortality, shortened life-span, impairment of bodily function, sensitization to chemicals in the environment, or diminished ability to reproduce. Exposure denotes the magnitude and the length of time the organism is in contact with an environmental contaminant, including chemical, radiation, or biological contaminants. When risk is in term of probability, it is expressed as a fraction, without units. It has values from 0.0 (absolute certainty that there is no risk) to 1.0 (absolute certainty that an adverse outcome will occur). There are four components of risk assessments, which are hazardous assessment, dose-response, exposure assessment, and risk characterization.

The waste management hierarchy is defined as follows (Allen and Shonnard, 2002): pollution should be prevented or reduced at the source whenever feasible; pollution that can not be prevented should be recycled in an environmentally safe manner, whenever feasible; pollution that can not be prevented or recycled should be treated in an environmentally safe manner whenever feasible; and disposal or other release into the environment should be employed only as a last resort and should be conducted in an environmentally safe manner. Based on this definition the waste management hierarchy in the descending order is source reduction, in-process recycle, on-site recycle, off-site recycle, waste treatment, secure disposal and direct release to the environment. Process design modification for pollution prevention will constitute the first four elements of the waste management hierarchy.

Fugitive emission sources, which are valves, pumps, piping connectors, pressure relief valves, sampling connections, compressor seals, and open-ended line, are significant contributors to air pollution from synthetic organic chemical manufacturing industrial facilities. Allen and Shonnard (2002) pointed out that as much as one third of air emissions occur from fugitive sources. Their major modeling approach to estimation of environmental fates of emissions and wastes is to use multimedia compartment models, which predict chemical concentrations in several environmental compartments simultaneously.

The metrics for environmental risk evaluation of process designs are shown in Table 2-20. The goal of design activity, called byproduct synergy, zero waste systems, or even industrial ecology, is to create industrial systems that are as mass efficient and tightly networked as possible.

Table 2-20 Environmental Impact Index Categories for Process Flow-Sheet Evaluation, from Allen and Shonnard (2002)

Abiotic Indexes	Health-Related Indexes	Ecotoxicity Indexes
Global warming	Inhalation toxicity	Fish aquatic toxicity
Stratospheric ozone depletion	Ingestion toxicity	
Acid deposition	Inhalation carcinogenicity	
Smog formation	Ingestion carcinogenicity	

In general green chemistry and green engineering have strong relationships with global sustainability. Verbound, loosely translated as integrated systems, is a networking approach that combines isolated company functions with social interests in product development to improve overall efficiency. Verbound was started at BASF's Ludwigshafen and has spread to BASF sites worldwide. Verbound in some ways is similar to the Six Sigma business-improvement process, which has made inroads in major U.S. businesses, such as Motorola, Dow Chemical, Dupont and General Electric (Ritter, 2001). Six Sigma is a company-wide effort to reexamine projects to discover the root causes of problems with the idea of optimizing a product to make it better. Ritter (2001) brought forward that Verbound, Six Sigma, the chemical industry's Responsible Care program, and the triple bottom-line business strategy that combines a commitment to profit, ecology and social responsibility are all concepts that share the goals of at least some parts of twelve principles of green chemistry presented by

Anastas and Warner (1998). All of these concepts are needed to meet the target of global sustainability.

In summary, green chemistry and green engineering have the same goals to get to sustainable development, where chemists and chemical engineers coordinate efforts in order to get the best way to serve the society.

C-5. Ways to Sustainability

For sustainable development there are different opinions on how to deal with pollution control and how to reach sustainability. Hogue (2001a) stated EPA assessed economic benefit fines to remove any financial incentive for violating environmental regulations using BEN model. BEN is the EPA computer model to calculate the economic benefit of a pollution control violation. She also stated that Susan Dudley, deputy director of the Regulatory Studies program at Mercatus Center of George Mason University, does not support the concept of fines to capture a company's economic benefit from a violation because it is not providing incentives to try to minimize environmental harm. Instead she favors fines aimed at collecting the cost to society of a violation.

Clarke (2001) provided a refinery LP-model-based CO_2 management methodology. The CO_2 refinery LP model optimizes the various options available and selects the optimal route to be used according to economic optimization criteria. The model can be run with fixed emissions targets (a process constant) or with an economic incentive (an economic constraint) on capturing CO_2 or avoiding its emission. Refinery options include avoiding production of CO_2 in the first place, vs capturing CO_2 after emission.

There are different names and ranges for sustainable cost of carbon. For example, energy industries employ “shadow” price for carbon to measure the cost. A shadow price in the range of \$5 to \$40 per ton of carbon reflects a broad range of potential damages from the increase of greenhouse gas concentrations in the atmosphere highly dependent on assumptions about discount rate and damage function (World Bank, 1996). Greenhouse gas emissions will be converted to equivalent carbon emissions with factors determined by the Intergovernmental Panel on Climate Change (IPCC). Equivalent carbon emissions for carbon dioxide are calculated by multiplying the change in carbon dioxide emissions by 12/44, the molecular weight ratio. For methane, the equivalent carbon emissions are calculated by multiplying the emissions by the global warming potential (approximately 24.5 on a mass basis) to convert methane to carbon dioxide and then by 12/44 to convert to equivalent carbon.

Emission-trading is a mechanism for lowering the cost of meeting environmental performance goals. Emission-trading lowers the cost of meeting emissions limits in three ways. The first is that trading allows companies with low-cost emissions reduction opportunities to reduce their emissions below the limits prescribed by the cap, then sell their surplus reduction to companies facing limits whose reduction costs are higher. The second is that by creating financial incentives for companies that lower their emissions, in the form of a market for surplus reductions, emissions-trading spurs the development of new emissions control technologies and techniques. The third is that creative new approaches to emissions prevention are encouraged because emissions trading gives business flexibility with regard to how they meet their emission limits. The critical advantage of emissions trading is that it allows society to get more pollution prevention for every dollar spent on emissions reductions.

Hogue (2002) reported that the European Union would commence the world's first international emission trading system for greenhouse gases in 2005. The penalty rate for the period 2005-2007 would be 40 euros per metric ton of CO_2 emissions not covered by allowance. This penalty would rise to 100 euros per metric ton in 2008. The EU would eventually add other greenhouse gases, such as methane, to its trading effort. One drawback was participation would be voluntary (Franz and Ondrey, 2003). For example, the Chicago Climate Exchange with 14 founding members was launched in January 2003 as a voluntary cap-and-trade program for CO_2 and other greenhouse gases.

The Environmental Resources Trust Inc. (ERT) is developing the GHG (greenhouse gas) Registry ^{SM} and associated services to support the key infrastructure requirements needed for a robust GHG emissions reductions trading market. For a carbon trading system to operate effectively, there needs to be: effective emissions monitoring and reporting by participants; independent verification of emissions; and an enforcement mechanism. For example, greenhouse gas value is between \$5 and \$35 per ton of carbon in the USA, Canada and Costa Rica.

Hogue (2001b) gave the current state of the U.S. government views on the strategies to control SO_2, NO_x, mercury, and maybe CO_2. At least three substances, i.e. sulfur dioxide, oxides of nitrogen, and mercury, should be in the multiple-pollutant approach to regulating air emissions. And these so-called cap-and-trade programs would work well for most of the power plant pollutants, especially for SO_2. People argued against including CO_2 in a multipollutant bill for CO_2 has never been classified as a pollutant by the Clean Air Act and does not pose any direct threat to human health, unlike NO_x, SO_2 and mercury. Hileman (2002) reported that although the Bush administration had refused to join the international efforts to reduce greenhouse gas emissions, more than half the states had policies to reduce greenhouse gases.

If the Kyoto Protocol goes into force, it will result in binding limitations in the so-called “Annex I” countries: thirty-nine developed countries and countries with Economies-In-Transition (EITs). These Parties agreed to ensure that their aggregate GHG emissions do not exceed their assigned amount. The Protocol would institute legally binding emission levels on six greenhouse gases, i.e., CO_2, CH_4, N_2O, HCFs, PFCs, SF_6. The Protocol will provide for possible carbon emissions trading among Annex I countries. On the other hand, equity is of the fundamental concern in the quest of international cooperation to stabilize greenhouse gas concentrations by emission reduction and emission trading, which is presented by Bolin and Kheshgi (2001).

Resources For The Future (2001) talked about some changes made to the Kyoto Protocol in July 2001, in Bonn. There are several new agreements among participants, such as no quantitative limits placed on permit trading and there is an upper bound for the use of biological sinks. The protocol did not specify any legally binding consequences to enforce compliance with these commitments, such as financial penalties. Hence permits in the market are nothing more than highly speculative investment because uncertainty over compliance leads to uncertainty over the value of permits. The conclusion is that the protocol lays a very poor foundation for a robust international market in GHG, if this kind of market is the best way to get cost-effective GHG control.

Sonneborn (2001a), from an Australian perspective, talked about the different responses to the carbon trading. There is a growing awareness that GHG issues have moved beyond the scientific debate. The economic impacts and the need to quantify these are essential before concerted action can take place. Multiple benefits of GHG response are desired by industry. And the assurance from the government and the community are also engaged. The best way to categorize the current mood among resource companies is a “wait and see” approach.

Sonneborn (2001b) also talked about Renewable Energy (RE) as a CO_2 solution. The early development of RE technologies is as a response to global warming. This development is in the economic interest of the world in the carbon trading market. RE companies can benefit by building partnerships with companies that will be required to reduce their CO_2 emissions.

Also similar to carbon trading, a sulfur dioxide (SO_2) emission-trading program proposed by former President Bush, is part of the 1990 Clean Air Act

Amendments. This program is very successful. Based on that Burtraw (2001) recommended that the method to allocate allowance is the most important for the efficiency of a trading policy. There are three methods to allocate the emission allowance in the electricity sector, which is very relevant for an economy-wide program. The first is called revenue-raising auction where the auction can be coupled with a cap or safety valve on the maximum price for allowances, and this approach is also called the Sky Trust proposal after a group by that name formed to advocate this approach. The second is called grandfathering where allowances will be distributed on the basis of historic generation, derived from the SO_2 trading program. The third is named Generation Performance Standard (GPS) which is from legislative proposals and nitrogen oxide (NO_x) policy in Sweden, where allowance will be distributed on the basis of shares of current electricity generation. He concluded that revenue-raising auction is much more cost-effective than the others, roughly 50% cheaper than each of them, which means reducing CO_2 in an auction approach will have less effect on economic growth than the other two and this approach provides the best form of distributional benefit. But he also pointed that for the deployment of an auction approach, a hybrid program that combined an auction with a GPS or grandfathering should be used in a transition period, and ultimately this hybrid approach will be replaced by an auction.

Just like carbon trading to control the greenhouse emissions, nutrient trading is to improve water quality. Hennessy (2001) introduced NutrientNet (http://www.nutrientnet.org/prototype/html/index.html), which is an online market and information tool to support regional nutrient trading, which is seen as a promising way to meet water quality goals cost effectively within a Total Maximum Daily Load requirement of the Clean Water Act. The trading aims at phosphorous and nutrient reduction when the waters are becoming eutrophication and hypoxia, which becomes dead zones, for example the areas of the Gulf of Mexico and the Chesapeake Bay are well-known dead zones and they are becoming larger and larger. There are two types of traders, one is point-source facility, such as municipal wastewater treatment plant or phosphoric acid plant, which is regulated by discharge permits; the other is non-point sources, such as agriculture land, which is unregulated. Hence, there are two general ways for the trading, namely, a point-source and another point-source or a point-source and a nonpoint-source. Therefore, the nutrient trading can also be considered in the total cost analysis, especially for the agricultural chemical production.

While industries strive for sustainability, agriculture faces the same sustainable problem in reducing the risk of global warming. Reese (2001) stated that Australia farmers are taking part in a methane vaccine program whose idea is to reduce the animals' emissions of methane, a GHG, and thus slow global warming and offer possibility of labeling and marketing sheep and cattle as environmentally friendly and sustainable enterprise. As a GHG, methane is around 21 times more potent than carbon dioxide. Sheep and cattle produce about 14% of Australia's total greenhouse emissions, measured in CO_2 equivalents.

Thayer (2001) stated that the benefits for U.S. farmers to plant genetically engineered crops outweigh the risks. The environmental pollution is reduced from reduced use of insect and herbicide pesticides.

In summary, there are many ways to get to sustainability, especially according to Kyoto Protocol there is an emission-trading system. Since GHG is the important factor for climate change, there should be emission-trading systems, such as carbon-trading system, to reduce GHG emissions, or sustainable cost will be charged on carbon emissions. Also SO_2 emissions-trading system is a successful example. In addition to get to sustainability, other emissions should be reduced by some systems, such as nutrient trading system. Industrial ecosystem and industrial park could be better ways for some regions. Sustainable development is expanding from industries to agriculture, and finally to every line of business.

D. CO_2 Utilization

There is an excess of 120 million tons per year of carbon dioxide from the exponential growth of ammonia production in the last 30 years (Moulijn, et al., 2001). Song (2002) estimated the potential upper limit of carbon dioxide use as a raw material, where the total of 650 million metric tons of CO_2 included traditional processes for urea and methanol in addition to plastics, fibers, rubber and other uses.

No single new technology will solve the entire problem of the carbon dioxide emission reductions (Flannery, 2001). All of them have to overcome challenges of economics, performance, and associated environmental impacts which are some of the barriers identified to be able to make a new technology into widespread commercial use (Flannery, 2001). For example, the costs involved for CO_2 capture from a manufacturing process, its separation and purification from the gaseous mixture, and energy requirements for CO_2 conversion are some of the main challenges being faced for the CO_2 utilization (Song, 2002). Most commercial plants capturing CO_2 from power plant flue gas use is based on chemical absorption with monoethanolamine (MEA) solvent. There are not many power plants use this method because these processes are expensive due to the amount of energy needed to regenerate the absorbent, about \$150 per ton of carbon (Hairston, 2004). In addition, MEA has some problems, such as relative low absorptivity for CO_2, corrosiveness and decomposition. Hence, the goal of many research efforts is the search for the viable MEA alternatives. There are physical and chemical absorption processes for separation of CO_2 (Table 2-21).

Table 2-21 Separation of CO_2, from Aresta and Forti (1986)

Physical absorption	Chemical absorption
CH_3OH (Rectisol)	
Molecular sieve (Union Carbide)	Monoethanol amine
Membrane (Enstar Eng. Co.)	Diethanol amine
Dimethylether of polyethylene glycol (Selectol)	Triethanol amine
Gas/Spec (Dow Chem.)	CO_2 acceptor: $CaO + CO_2 \rightarrow CaCO_3$
Propylene carbonate NMP (Purisol/Lurgi)	
Sulfinol (Shell)	

The utilization of CO_2 is based on its properties, such as solubility, reactivity, inertness and non-toxic. CO_2 is generally considered as a green and environmentally benign solvent because it is nontoxic, nonflammable and natural abundant, which is regarded as a sustainable replacement for organic solvents in some chemical processes.

Aresta (1997) categorized CO_2 uses from three different viewpoints as follows. From environmental issues view, CO_2 can be used as solvents in the form of supercritical or liquid; building block for organic carbamates-isocyanates-cabonates to replace phosgene, and for carboxylates to avoid multistep procedures; carbon source in the synthesis of fuel instead of using CO or coal. From energetic point the reactions of CO_2 uses have two types. One is reactions where the entire CO_2 molecule is used with small amount extra energy input, such as carboxylation; the other is reduction reactions where C_1 or C_n species is formed with extra energy in the form of electrons and/or hydrogen. From the species formed based on their uses, there are two types of CO_2 uses: one is for intermediates or fine chemicals for the chemical industry, such as –COO-, -O-COO-, and –NCO; the other is for the products for the entire industry, such as CO and methanol. He concluded that it is a promising way to use CO_2 in synthetic chemistry for creating benign synthetic methods to avoid toxic species and saving energy and carbon.

Arakawa, et al. (2001) reviewed the current status of CO_2 utilization. Also there is another abstract about CO_2 as a feedstock (National Research Council, 2001b). About 110 megatons of CO_2 are used annually for the chemical synthesis. Now the commercial chemical synthesis from CO_2 are urea, salicylic acid, cyclic carbonates and polycarbonates, among which urea production is the largest with about 90 megatons in 1997. Salicylic and cyclic organic carbonate is used for polyacrylic fibers and paints. Generally CO_2 can be used as a carbon source or an oxygen source. The detailed utilization of CO_2 is listed in Table 2-22, with some new reactions and reaction conditions for CO_2 in Table 2-23.

Table 2-22 Chemical Synthesis from CO_2

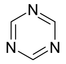
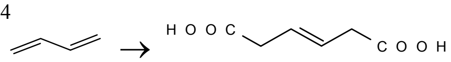
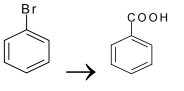
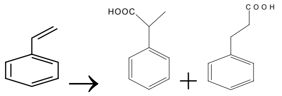
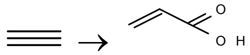
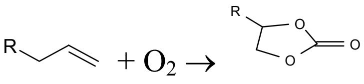
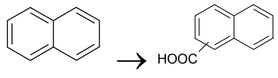
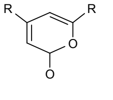
CO_2 hydrogenation
$CO_2 + H_2 \rightarrow CH_4$ $CO_2 + H_2 \rightarrow C_nH_{2n+2}$ or C_nH_{2n} $CO_2 + H_2 + NH_3 \rightarrow C_nH_{2n+1}NH_2$ or $HCONH_2$ or  $CO_2 + H_2 + HY \rightarrow HCOY + H_2O$ $CO_2 + H_2 \rightarrow C + H_2O$ $CO_2 + H_2 \rightarrow CH_3CH_2OH$
CO_2 electrochemical reaction
$CO_2 + 2e^- + 2H^+ \rightarrow HCOOH$ $CO_2 + 2e^- \rightarrow CO$ $CO_2 + 4e^- + 4H^+ \rightarrow CH_3OH$ $CO_2 + 4e^- + 4H^+ \rightarrow CH_4$ $CO_2 + 12e^- \rightarrow C_2H_4$ $CO_2 + 2e^- + 2H^+ +$  $CO_2 + 2e^- + 2H^+ +$  $CO_2 + 2e^- + 2H^+ +$  $CO_2 + 2e^- + 2H^+ +$ 
CO_2 carboxylation (CO_2 insertion)
$CO_2 + ROH + R_2NH \rightarrow HCOOR + HCONR_2$ $CO_2 + C_2H_4 + H_2O \rightarrow CH_3CH(OH)COOH$ $CO_2 + C_6H_5ONa \rightarrow C_6H_5(COONa)OH$ $\xrightarrow{H^+} C_6H_5(COOH)OH$ $\xrightarrow{(CH_3CO)_2O} C_6H_5(COOCH_3)COOH$ $CO_2 +$  $CO_2 +$  $CO_2 +$ RC≡CR →  $CO_2 + RNH_2 + R'X \rightarrow RNHCOOR'$

Table 2-22 Continued

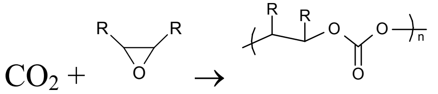
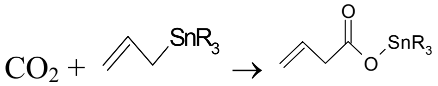
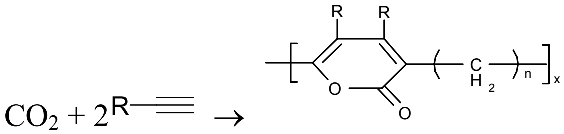
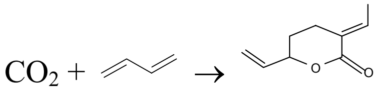
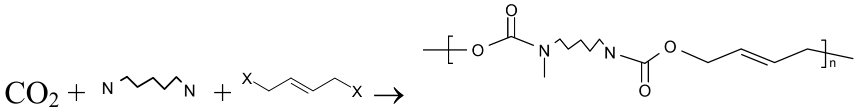
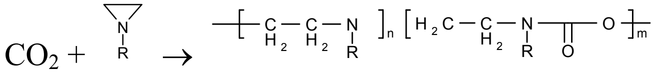
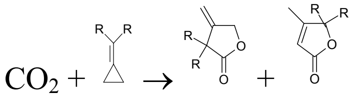
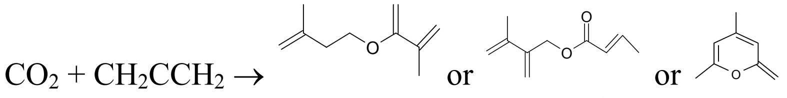
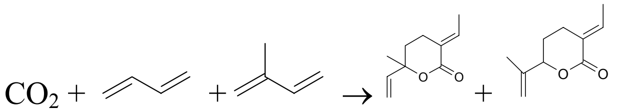
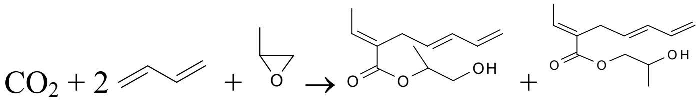
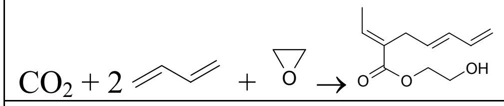
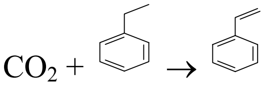
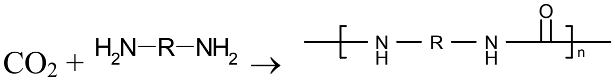
CO_2 carboxylation (CO_2 insertion) (Continued)


$CO_2 + CH_4 \rightarrow CH_3COOH$
$CO_2 + ROH \rightarrow ROCOOR$




$CO_2 + M\text{-}R \rightarrow RCOOM$

$CO_2 + C_2H_4 \rightarrow CH_3CH_2COOH + CH_3CH_2COOC_2H_5$




CO_2 used as oxidant (oxygen provider)
$CO_2 + C_3H_8 \rightarrow C_3H_6$
$CO_2 + CH_4 \rightarrow CO$
$CO_2 + 2NH_3 \rightarrow CO(NH_2)_2 + H_2O$

Table 2-22 Continued

CO_2 used as oxidant (oxygen provider) (Continued)



Note: M – metal; X- haloid element; HY- H_2O, KOH, ROH, HNMe; R, R'-alkyl radical

Table 2-23 New Reactions of CO_2

CO_2 Reactions and Reaction Conditions
$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ methanol • Raney Cu-Zr catalyst, flow reactor, 523 K, 5 MPa, $CO_2/H_2 = 1/3$, SV = 18,000h^{-1}, methanol activity 941 mg-MeOH/ml-cat·h, (Toyir, et al., 1998). • Pd promoted $Cu/ZnO/Al_2O_3$ catalyst, internal recycle reactor (300 cm^3 volume, 100 cm^3 catalyst basket), 5 MPa, 250°C, $H_2/CO_2 = 4/1$, flowrate is larger than 240 ml/min (s.t.p.), methanol selectivity about 58-65% (Sahibzada, et al., 1998). • Production capacity 50 kg/day, multicomponent catalyst $Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3$, tube reactor, 523K, 5 MPa, $H_2/CO_2 = 4/1$, SV = 10,000h^{-1}, high selectivity with the purity of methanol 99.9%, methanol production rate 600 g/l-cat·h (Ushikoshi, et al., 1998). • Ru promoted Cu-based catalyst (CuO-ZnO/TiO_2), conventional continuous flow reactor, 1.0MPa, 553 K, molar ratio $H_2/CO_2 = 4/1$, $W/F_{CO_{2,0}}$ = 570 kg-cat·s/mol, 7.7% conversion, 20.4% selectivity (Nomura, et al., 1998). • Hybrid catalyst of $Cu/ZnO/Cr_2O_3$ and CuNaY zeolite, fixed bed micro-reactor, 523K, 30 kg/cm^2, $H_2/CO_2 = 3/1$, flow rate = 30 ml/min, conversion to methanol and dimethyl ether (oxygenates) = 9.37%, dimethyl ether selectivity in oxygenates = 36.7% (Jun, et al., 1998). • Cu/ZnO-based multicomponent catalyst ($Cu/ZnO/ZrO_2/Al_2O_3$) modified with the special silicone oil (5wt%), liquid-phase continuous reactor, 523K, 15MPa, $H_2/CO_2 = 3/1$, recycle rate of solvent = 100 l-solvent/l-cat/hr, 650 g-MeOH/kg-cat/hr (Mabuse, et al., 1998). • Cu/ZnO catalyst (Cu/ZnO = 50/50wt%), flow type fixed bed reactor, 250°C, 5MPa, $H_2/CO_2 = 3/1$, SV = 26,000hr^{-1}, methanol synthesis activity = 350 g/l-cat·h about 1.5 times higher than that over conventional coprecipitated Cu/ZnO catalyst (Fukui, et al., 1998). • Ca addition Pd/SiO_2 catalyst, microreactor, 3.0 MPa, 523K, $H_2/CO_2 = 3/1$, SV = 10,000h^{-1} (Bonivardi, et al., 1998).

Table 2-23 Continued

CO_2 Reactions and Reaction Conditions (Continued)
$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ methanol (Continued) • Pd-modified composite catalyst (38.1% Cu, 29.4% ZnO, 1.6% Cr_2O_3, 13.1% Al_2O_3, 17.8% Ga_2O_3), pressurized reactor, $270^\circ C$, 80 atm, SV = 18,800h^{-1}, $CO_2/CO/H_2$ = 22/3/75, conversion to methanol = 22% (Hara, et al., 1998a). • $Cu/ZnO/Al_2O_3$ catalyst, packed-bed reactor, H_2/CO_2 = 3/1, 20 bar, $220^\circ C$, SV = 4,500h^{-1}, methanol yield = 7.1% per single pass, selectivity = 43.8% (Bill, et al., 1998). • Cuo-ZnO-Al_2O_3 catalyst (Al_2O_3 5wt%), microreactor, 513-521K, 9MPa, H_2/CO_2 = 3/1, GHSV = 5,000h^{-1}, recycle ratio = 4m^3N/m^3N, methanol yield = 95% for 3,000 hours (Hirano, et al., 1998).
$2CO_2 + 6H_2 \rightarrow C_2H_5OH + 3H_2O$ ethanol • 5 wt% Rh/SiO_2 catalyst, a pressurized fixed-bed, flow-type micro-reactor, 533K, 5 MPa, H_2/CO_2 = 3/1, flow rate = 100cm3/min, ethanol selectivity = 2.0% (Kusama, et al., 1998). • Li/RhY catalyst, fixed bed flow reactor, 523K, 3MPa, H_2/CO_2 = 3/1, 10ml/min, ethanol selectivity = 16% (Bando, et al., 1998). • Pd- modified Cu-Zn-Al-Kmixed oxide combed with the Fe-based catalyst, 330°C, 80atm, CO_2/H_2 = 1/3, SV = 20,000h^{-1}, the space yield of ethanol = 476 g/l·h (Yamamoto and Inui, 1998). • Conventional flow reactor, K/Cu-Zn-Fe-Cr oxides catalyst, 300°C, 7.0MPa, 35% CO_2 conversion and 16% ethanol selectivity (Higuchi, et al., 1998). • Conventional flow reactor, K/Cu-Zn-Fe oxides catalyst, 300°C, 7.0MPa, GHSV 5,000, H_2/CO_2 = 3/1, CO_2 conversion 44% and ethanol selectivity 20C-% (Takagawa, et al., 1998).
$2CO_2 + 6H_2 \rightarrow CH_3OCH_3 + 3H_2O$ dimethyl ether • Hybrid catalyst of Cu/ZnO/Cr_2O_3 and CuNaY zeolite, fixed bed micro-reactor, 523K, 30 kg/cm^2, H_2/CO_2 = 3/1, flow rate = 30 ml/min, conversion to methanol and dimethyl ether (oxygenates) = 9.37%, dimethyl ether selectivity in oxygenates = 36.7% (Jun, et al., 1998).
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ methane and higher hydrocarbons • Amorphous Ni-Zr-rare earth element catalyst (Ni-30Zr-10Sm), fixed bed flow reactor, CO_2/H_2 = 1/4, F/W = 5,400 ml·$g^{-1}h^{-1}$, 473K, CO_2 conversion = 98% with water removal (Habazaki, et al., 1998). • Fixed bed reactor, Fe/HY catalyst, 573K, 10atm, H_2/CO_2 = 3/1, CO_2 coversion 3.15%, CH_4 distribution in hydrocarbons = 75.70% (Kim, et al., 1998). • Fe-Cu-Na with US-Y catalyst, 250°C, 20atm, SV = 3,000 ml/g-cat/h, H_2/CO_2 = 3 /1, CO_2 conversion = 12.5%, 35.1 C-mol% conversion to CH_4 (Xu, et al., 1998).

Table 2-23 Continued

CO_2 Reactions and Reaction Conditions (Continued)
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ methane and higher hydrocarbons (Continued) • Fe promoted Cu-base catalyst, conventional flow reactor, 553K, 1MPa, H_2/CO_2 = 4/1, $W/F_{CO2,0}$ = 570kg-cat·s/mol, CO_2 conversion = 23.4%, selectivities for CH_4, C_2H_6, C_3H_8 and C_4H_{10} were 17.3%, 6.6%, 5.8% and 4.6% (Nomura, et al., 1998). • Fixed-bed flow reactor, Fe-Zn-Zr/HY catalyst, 360°C, 5MPa, SV = 3,000 ml/g-cat/h, H_2/CO_2 = 3/1, CO_2 conversion = 17.2%, hydrocarbon selectivity = 46.8%, iso-butane yield = 3.0C-mol% (Tan, et al., 1998).
$2CO_2 + 6H_2 \rightarrow C_2H_4 + 4H_2O$ ethylene and higher olefins • Fixed bed flow reactor, Fe-ZnO/HY catalyst, 350°C, 50 atm, SV = 3,000ml/g-cat·h, H_2/CO_2 = 3, 6 hours, CO_2 coversion = 13.3%, C_{2+} yield = 4.5, ethylene selectivity = 90% (Souma, et al., 1998). • Fixed bed reactor, Fe-K/HY catalyst, 573K, 10atm, H_2/CO_2 = 3/1, CO_2 coversion 21.28%, C_2H_4 distribution in hydrocarbons = 9.12%, olefins selectivity = 82.38 C-mol% (Kim, et al., 1998). • Fe-Cu-Na catalyst, 250°C, 20atm, SV = 3,000 ml/g-cat/h, H_2/CO_2 = 3/1, CO_2 conversion = 6.8%, olefin ratio in the group of olefin and paraffin = 70.5% (Xu, et al., 1998).
$CH_4 + CO_2 \rightarrow CH_3COOH$ acetic acid • Autoclave, $VO(acac)_2$ catalyst, $K_2S_2O_8$ and CF_3COOH were added, 80°C, 5 atm CH_4, 20 atm CO_2, turnover number = 18.4, acetic acid yield based on CH_4 = 97% (Taniguchi, et al., 1998).
$CO_2 + H_2 \rightarrow HCOOH$ formic acid • Autoclave, Rhodium catalyst, 25°C, 40 bar, H_2/CO_2 = 1/1, 12 hours, 3440 mol formic acid per mol Ru (Dinjus, 1998).
$2CH_4 \rightarrow 2C + 4H_2$ $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ Total: $CH_4 + CO_2 \rightarrow 2C + 2H_2O$ graphite • Membrane reactor, nickel supported on SiO_2 catalyst, 500°C, 70% CO_2 reduced to graphite carbon (Nishiguchi, et al., 1998).
CO_2 photoelectrical chemical and electrical chemical reactions $CO_2 \rightarrow CO + CH_4 + C_2H_4 + CH_3OH + HCOOH + C_2H_5OH + CH_3CHO$ • ZrO_2-modified, periodically activated, Cu electrode in 0.5 M K_2SO_4, 5°C, E = -1.8V, faradaic efficiencies for CH_4, C_2H_4 and C_2H_5OH were 4%, 33% and 12% at 90 minutes. (Augustynski, et al., 1998).

Table 2-23 Continued

CO_2 Reactions and Reaction Conditions (Continued)
CO_2 photoelectrical chemical and electrical chemical reactions (Continued) • A functional dual-film electrode consisting of Prussian blue and polyaniine doped with a metal complex, solar cell, CO_2 in aqueous solution to produce lactic acid, formic acid, methanol, the maximum current efficiency for the CO_2 reduction was more than 20% at –0.8V vs Ag | AgCl (Ogura, et al., 1998). • Gas diffusion electrode (GDE) of (CuO/ZnO = 3/7) : carbon black = 6 : 5 (by weight), 25°C, the reduction products were mainly C_2H_5OH with slightly amounts of CO and $HCOO^-$, and a comparable amount of H_2, faradaic efficiency of 16.7% for C_2H_5OH formation with 88% selectivity at –1.32 V vs. Ag-AgCl (Ikeda, et al., 1998). • CdS photocatalyst in acetonitrile, irritated with light of wavelengths longer than 300 nm, fraction of HCOOH in products = 75% with CO 20% (Torimoto, et al., 1998). • Ti/Si binary oxide catalyst, a quartz cell connected to a coventional vaccum system, UV irradiation, 328K, CO_2 and H_2O as reactants, methane and methanol as main products, CH_3OH selectivity = 22 mol% on the binary oxide at 1 wt% as TiO_2 (Yamashita, et al., 1998). • Particulate-Cu/p-Si electrode, 20°C, pure CO_2, 0.50-0.75V, current efficiencies of CO, HCOOH, CH_4 and C_2H_4 were 20.8%, 6.6%, 2.1%, 4.7%, respectively (Nakamura, et al., 1998). • Pulsed electrolysis of CO_2 on Au, Ag, Cu and their alloyed electrodes, 10°C, typical faradaic efficiencies on Cu electrode for CH_4, C_2H_4, C_2H_5OH, CH_3CHO and HCOOH were 20.1%, 5.8%, 8.2%, 11.0% and 6.1% with total 87.4% (Shiratsuchi, et al., 1998). • Autoclave, high purity CO_2, by using Pt supported GDEs in reverse arrangement methane was produced at faradaic efficiency of 38.8%; by using Ag and Pd supported GDEs, CO was produced at faradaic efficiency of 57.5-86.0% (Hara, et al., 1998b).
$CH_4 + CO_2 \rightarrow 2CO + 2H_2$ reforming to CO • Nickel-magnesia solid solution catalyst ($Ni_{0.03}Mg_{0.97}O$), fixed bed flow reaction system, CH_4/CO_2 = 1/1, 1,123K, 0.1MPa, W/F = 1.2 gh/mol, methane conversion = 80% (Tomishige, et al., 1998). • KNiCa/ZSI catalyst, 700°C, reaction scheme was described (Park, et al., 1998).
$C_6H_5C_2H_5 + CO_2 \rightarrow C_6H_5C_2H_3 + CO + H_2O$ styrene • Zeolite-supported iron oxide catalyst, conventional flow-type reactor, 873K, 1atm, CO_2/EB (ethylbenzene) = 80, W/F = 298 g·h/mol, EB conversion = 40%, styrene selectivity = 40% (Chang, et al., 1998). • Fe/Ca/Al oxides catalyst, 580°C, 1 atm, CO_2/EB = 9/1, styrene selectivity = 70%, energy requirement = $6.3x10^8$ cal/t-styrene (1.5×10^9 cal/t-styrene for commercial process using steam) (Mimura, et al., 1998).

Table 2-23 Continued

$CO_2 + C_3H_8 \rightarrow C_3H_6 + CO + H_2O$ dehydrogenation of propane to propylene

- Cr_2O_3/SiO_2 catalyst, fixed bed flow reactor, 823K, 1atm, $C_3H_8/CO_2 = 1/1$, W/F = 2g-cat·h/mol, C_3H_6 yield = 9% at 0.33 hour (Takahara, et al., 1998).

Song (2002) described that for chemicals having large market and demand, developing new and alternate processes where carbon dioxide can be utilized as a reactant or co-feed is an effective way to increase the utilization of carbon dioxide. As global warming becomes more severe and the fossil fuels will be depleted, energy sources will have to be changed from fossil fuels to renewable and nuclear energy. CO_2 can be reduced to methane, methanol, and other carbon based fuel by the new energy sources. This will have no net CO_2 increase in the atmosphere, which have a very good reduction on CO_2 emission.

CO_2 can react with metal salts to metal carbonate, such as Na_2CO_3, K_2CO_3, $BaCO_3$ and pigments in inorganic utilization (Aresta and Forti, 1986). Almost all of CO_2 utilization is in organic processes (Table 2-22 and Table 2-23), such as the production of aspirin.

$$
\begin{aligned}
&CO_2 + C_6H_5ONa \rightarrow C_6H_5(COONa)OH \\
&\qquad \xrightarrow{H^+} C_6H_5(COOH)OH \quad \text{salicylic acid} \\
&\qquad\qquad \xrightarrow{(CH_3CO)_2O} C_6H_5(COOCH_3)COOH \quad \text{aspirin}
\end{aligned}
$$

Methanol, CO, formic acid, N,N-dimethylformamide (DMF) and lower hydrocarbons, such as methane, ethane, ethylene, have been prepared from CO_2 and H_2 using different catalysts at elevated temperature and pressure, where hydrogen may be replaced by electrons and protons.

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

Dimethyl ether (DME) is produced directly from CO_2 and hydrogen, by producing methanol first then dehydrating methanol to DME by KEP company (Chemical Engineering, 2001). KEP has achieved 90% CO_2 conversion and 45% DME selectivity.

$$\mathrm{CO_2 + 3H_2 \rightarrow CH_3OH + H_2O}$$
$$\mathrm{2CH_3OH \rightarrow CH_3OCH_3 + H_2O}$$

By using the new catalysts, a chromium (III) bis(salicylaldimine) complex as catalyst and 4-dimethylaminopyridine as co-catalyst, a variety of terminal epoxides, such as aliphatic and aromatic epoxides and epichlorohydrin, can react with CO_2 to produce corresponding cyclic carbonates in near quantitative yield and 100% selectivity without side product or waste (C & EN, 2001).

In some processes carbon dioxide can replace the raw material or the reactant which is hazardous or not an environmentally benign chemical. For example, replacement of phosgene with carbon dioxide in the production of dimethyl carbonate is a good example in this category (Song, 2002).

Supercritical CO_2 is a hydrophobic solvent that can replace organic solvents in a number of applications. Currently CO_2 is used in caffeine extraction, dry cleaning and parts degreasing (Aresta and Forti, 1986). Its potential use is in food and pharmaceutical process, polymerizations, enhanced oil recovery, and homogeneous and phase separable catalysis.

The promising research areas for new utilization of CO_2 are: use CO_2 in new polymers and complexes; produce fuels from CO_2; try to replace phosgene with CO_2 as much as possible; deploy both homogeneous and heterogeneous catalysts in the processes of CO_2 utilization, such as polymerization, hydrogenation, electrochemical, photochemical processes and in supercritical CO_2; use electrochemical and photochemical electron sources in presence of proton sources instead of expensive H_2 in fast and stable processes.

Song (2002) reported that carbon dioxide can be used in enhanced recovery of oil and natural gas, enhanced coal bed methane recovery where the requirement for purity of carbon dioxide is low, with low processing costs for separation and purification.

In addition, CO_2 can be captured and sequestrated as a long-term storage of CO_2 in various reservoir locations with large capacities, such as geologic formations, ocean, aquifers, and forest (Song, 2002). But the costs for direct sequestering CO_2 in geological formations, oceans and natural systems have been summarized (Kim and Edmonds, 2000). They estimated the cost to range from \$120 to \$340 per metric ton of carbon equivalent, along with \$50 per ton of carbon equivalent by 2015.

In summary, CO_2 has inorganic and organic utilization according to its properties, where its organic utilization is very important. CO_2 can be reduced to carbon based fuel with a renewable energy resource. CO_2 utilization can lead to the reduction of CO_2 emission and alleviating global warming. There is a growing concern over carbon management, CO_2 conversion and utilization emphasizing the scope and potential for CO_2 reduction.

E. Nanotechnology

E-1. Introduction to Nanotechnology

Nanotechnology is potentially regarded as the next big wave from a technology perspective. There are many kinds of nanomaterials, such as fullerenes, carbon nanotubes, polymer nanocomposites, nanopowder, and nanostructured materials in biomedial, pharmaceutical and cosmetic applications. The NanoBusiness Alliance (NBA) industry association reports that more than 50 U.S. venture-capital firms are already investing in the nanotechnology and the grants from the government are large amount. The involvement of nanotech includes many large companies. For example, BASF, Dow Chemical, 3M, and Chevron are testing the waters in new materials by investing in start-ups either directly or through venture funds. The market size of nanotechnology may seem inflated by traditional materials, such as carbon black, titanium dioxide and catalysts, which are being awarded the nanomaterials label (Thayer, 2001). Figure 2.10 displays the different sides of nanobusiness, where the total number of companies is 110 and there are some overlaps between categories.

E-2. Properties of Nano-Materials

Coy (2001) regarded nanoparticles as the bricks and mortar upon which a large portion of the first wave of commercial nanotechnology will be built. Nanoparticles, 1-100 nm, have the properties of chemical, optical, mechanical, melting points, crystal structures and etc, which depends on their sizes and synthesis technique.

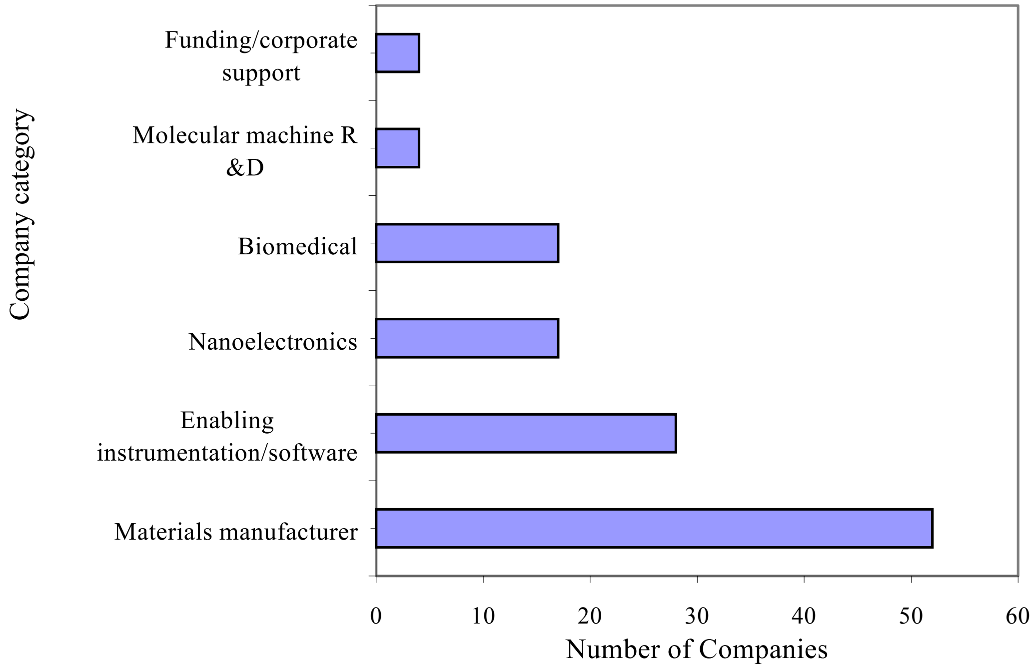


Figure 2.10 Nanobusiness Category, from Filmore (2001)

Meier (2001) introduced the structure of the Carbon NanoTubes (CNT). CNT are insoluble and the iron catalyst present in the core of the CNT makes the samples magnetic and inappropriate for solid-state NMR. The ideal model of CNT is that of a perfect graphene tube, with fullerene-like units composed of 5-membered rings as well as 6-membered rings. But in reality, there are numerous defects in CNT, which can be verified by experiments.

Shelley (2003) described single wall nanotube (SWNT) and multiple wall nanotube (MWNT). Individual SWNT can function as either metallic conductors or semiconductors, while every MWNT inevitably has a mixed suite of such properties, due to the alternating characteristics of its layered structure. Both SWNT and MWNT are being used as key components in the production of high-strength composites, and advanced sensors, electronics and optical devices, catalysts, batteries and fuel cells.

Fullerenes are the third form of carbon after graphite and diamond. Fullerenes have some unique properties, such as 1 nm diameter perfect spherical, large and protected internal cavity, high mechanical strength and electronegativity, soluble and chemically reactive.

E-3. Preparation of Nano-Materials

Shelly (2003) summarized that there were several technologies to produce carbon nanotubes: arc discharge, pulsed-laser vaporization, chemical vapor deposition, and several gas-phase processes, such as a high-pressure carbon monoxide process. She also reported that Hyperion Catalysis International, Inc. in Cambridge, Mass. claimed to be the world's only tonnage-scale producer of carbon nanotubes.

Motiei, et al. (2001) reported the two ways of the preparation of Carbon NanoTubes (CNT) discovered in 1991, physical methods and chemical methods. Generally physical methods are low energetic efficiency, low yield and high technical complexity, but the product quality is very good. Chemical methods are aimed at mass production with low energy consumption and reasonable yield, but low quality. He also introduced a new chemical method, which is that well-crystallized nanotubes from dry ice in the presence of Mg by heating the precursors in a closed vessel at the autogenetic pressure of the mixture.

Andrews and Jacques (2001) presented the development of the methods how to make nanotubes with the following examples. At first Maurico Terrones from Harry Kroto's group at Sussex created a simple and familiar system of carbon deposition in metal foils. Even if this method has good characteristics, such as high purity, low temperature and simple equipment requirement, the defects are very complicated process for the feed preparation. Based on this method, several other methods are found sequentially, and finally they can prepare nanotubes at the rate of 8 grams a day, along with the best way to maintain the simplicity and efficiency of making nanotubes.

Greene (2002) reported the process to produce fullerenes via a patented combustion synthesis, invented at M.I.T. in 1991, which can move fullerenes out of R & D and into commercial production with \$0.2/g instead of \$15-20/g. In this process C_{60} and C_{70} are formed in substantial quantities in the controllable ratio, along with C_{76}, C_{78}, C_{84} and larger. The product collection and separation are based on conventional technology.

In addition, Frontier Carbon Co. in Japan produces fullerene (hollow molecules of pure carbon), mainly C_{60} and C_{70} by burning a mixture of benzene or toluene with oxygen, under a reduced pressure and at 1000-2000^{o}C. Large-scale production will cut the price of fullerene to 1/100 of the existing price of \$50-60/g for research quantities. Carbon Nanotechnologies Inc. and Kellogg Brown & Root will commercialize single-wall carbon nanotubes or buckytubes, by injecting a gas-phase catalyst precursor of transition metals into carbon monoxide at about 100 bars and close to 1000^{o}C. The initial capacity will be 200-400 g/d.

For nanoparticles, the example of technology is physical vapor synthesis (PVS) and discrete particle encapsulation (DPE) reported by Coy (2001). In PVS, a plasma is used to heat a precursor metal whose atoms boil off to create a vapor. The vapor is cooled by a gas into liquid molecular clusters. The molecular clusters are frozen into solid nanoparticles during the cooling process. The metal atoms in the molecular clusters mix with oxygen atoms, forming metal oxides smaller than 100 nanometers, such as aluminum oxide. In DPE, two shells are added to nanoparticles, the insider is a thin polymeric shell around each nanoparticle; the out layer is a second thin-shell coating which contains spacer molecules that prevent the nanoparticles from coming into contact with each other. The product is steric stabilization for nanoparticles used in non-liquid solvents and polymers, and electrosteric stabilization for those needing to disperse in a fluid.

E-4. Uses of Nanotechnology

The nanoparticles can be used in health care, catalysts, functional coatings, fine polishing, ceramics, and etc. CNT have a lot of applications, such as being superconductors, single-molecular transistors and the part of magnetic recording devices after filled with metals or metal oxides.

Jacoby (2002) talked about the development on effective charge countering attractive forces between uncharged particles. Colloidal dispersions are very important in the industrial technologies. So the stability of suspensions of microscopic particles is necessary. As demand, highly charged nanoparticles, as a second component, can force uncharged or negligibly charged micrometer-sized particles into stable arrangements. This technique is based on Coulombic repulsion between the charged nanoparticles. Also by controlling the fraction of charged nanoparticles, colloidal fluid, gels, and crystals can be prepared respectively. In other words, there is a critical nanoparticle volume. However, the defect of charged particles does not have hydrophilic and hydrophobic characteristics.

Using electrochemical dip-pen nanolithography (E-DPN) to fabricate polythiophene nanostructures on semiconducting and insulting surfaces in the sub-100 nm regime is the emerging field for nanotechnology, presented by Maynor, et al. (2001). The monomer, 3,4-ethylenedioxythiophene (EDOT), is electrochemically polymerized at the interface by applying a voltage between the tip and the silicon wafer. The morphology is determined by the humidity, applied voltage and tip translation speed. Also this technique derives a method to deposit polymer and oxidize the Silicon surface simultaneously.

Withers, et al. (1994) summarized the applications of fullerenes, which include AIDS, HIV-1 and other virus control, hydrogen storage for fuels and batteries, non-linear optics, photoconductors, superconductors, precursors to diamond, carbon composites and fibers, and as a basis of three dimensional chemistry expected to surpass the utilization of benzene which is the well-known two-dimensional cage molecule. They also evaluated the fullerene production in MER Corporation in Arizona, whose material and energy costs accounted for only 14% of the total cost.

In summary, nano-materials have special properties and potentially broad applications. Nanotechnology will play an important role in the expended chemical industries as the technology develops.

F. Reaction Path Synthesis

Mathematical programming models for the synthesis of chemical process systems have got a lot of progress these years. Grossmann, et al. (1999) gave a detailed review of the advances taking place in this area associated with some examples, such as reactor networks, distillation sequences, heat exchanger networks and total flow sheets.

F-1. Logical Inference

Raman and Grossmann (1991) described the logical inference for reaction path synthesis that has the following formulation. In order to use mathematical programming to perform the inference procedure, all the reactions should be transformed into the propositional logic, then be converted into the corresponding conjunctive normal form, and finally changed into the equivalent mathematical representation.

First of all, express all the reactions in inference form by the basic operators, OR($\vee$), AND($\wedge$), IMPLICATION($\Rightarrow$). The basic unit of propositional logic expression standing for a state or an action is called a literal. A literal, for example P, is a single variable having either of two values, true or false, with the associated literal NEGATION P ($\neg$P). A clause is a set of literals separated by OR operators and is also called a disjunction. A proposition is any logical expression which consists of a set of clauses related by the logical operators AND, OR, IMPLICATION. For example,

$A + B \rightarrow C + D$ is expressed as $A \wedge B \Rightarrow C \wedge D$

Secondly, the propositional logic will be transformed into the corresponding conjunctive normal form by the three-step procedure raised by Clocksin and Mellish (1981).

1. replace the implication by its equivalent disjunction:

$$C \Rightarrow D \Leftrightarrow \neg C \vee D$$

2. move negation inwards using DeMorgan's Theorem:

$$\neg(C \wedge D) \Leftrightarrow (\neg C) \vee (\neg D)$$
$$\neg(C \vee D) \Leftrightarrow (\neg C) \wedge (\neg D)$$

3. recursively distribute the 'OR' over the 'AND':

$$(A \wedge B) \vee C \Leftrightarrow (A \vee C) \wedge (B \vee C)$$

Finally, the conjunctive normal form is converted into the mathematical representation, i.e. translate each clause into its equivalent mathematical linear form by assigning a 0-1 binary variable y to each chemical and converting all reactions into a set of the corresponding linear inequalities. For example,

$(\neg A \vee C \vee D) \wedge (A \vee \neg C \vee \neg D)$ becomes two linear inequality constraints

$$1 - y_A + y_c + y_D \geq 1$$
$$y_A + 1 - y_c + 1 - y_D \geq 1$$

After a set of linear inequalities have been created, the logical inference problem can be formulated as the MILP as follows:

If the general problem is presented as:

Prove P_u

s.t. $B(P_1, P_2, \ldots, P_q)$

MILP is:

$$Z = Min \sum_{i \in I(u)} c_i y_i$$

$$\text{s.t.} \quad \begin{array}{l} Ay \geq a, \\ y \in \{0,1\}^n \end{array}$$

where $Ay \geq a$ is the set of linear inequalities transformed from B(P_1, P_2, …, P_q); the objective function is obtained from P_u similarly; I(u) is the index associated with P_u. There are two possible results for the MILP. One is that Z=1, which means the clause P_u is always true on minimizing the objective function as an integer linear programming problem; the other is Z=0, which means the clause is not true on minimizing the objective function as an integer linear programming problem. Sometimes the relaxed LP can reach the conclusion if one of the following types come out:

1. $Z_{relaxed}$>0: the clause P_u is always true because Z is a lower bound to the solution.
2. $Z_{relaxed}$=0: if the solution is fractional and unique then the clause P_u is true; else no conclusion can be reached.

That the clause Pu is always true means the product can always be produced from the reactants whose value is 1. In other words, using logical inference the possibility of product to be produced and possible reaction path are determined.

Raman and Grossmann (1991) also described the problem about logical inference with uncertainty. There are two types of qualitative knowledge. One is called hard logical facts, such as the basic chemical principles; the other is uncertain heuristics that are just rules of thumb may not always holding. With modeling the violation of heuristics, the logical problem with uncertainty is formulated as an MILP problem, whose objective is to obtain a solution with the least total penalty for the heuristics violation.

$$\min Z = w^T v$$

$$\text{s. t. } Ay + v \geq a \text{ -----heuristics}$$

$$By \geq b \text{ ----------logical facts}$$

$$y \in \{0,1\}^n \text{ -------} v \geq 0$$

where v is for the violation of each heuristic rule; w is for the uncertainty of the corresponding logical expression. The solution of this model is the best design satisfying the possibly conflicting qualitative knowledge about the system. Logical inference with uncertainty are more often encountered than only logical inference in design and process synthesis to select the best flowsheet or design for producing the required product starting with the available raw materials.

F-2. Graph-Theoretical Identification

As for reaction-pathway determination, Fan, et al. (2001, 2002) presented graph-theory identification for the synthesis of reaction path, which is different from logical reference. They have successfully employed it on ammonia process and biochemical reactions (Fan, et al., 2001; Seo, et al., 2001). They defined two phases for reaction-pathway determination: the first is the identification of all feasible candidate mechanism; the second is selection of ultimate pathway or mechanism from those identified in the first phase. There are two sets of axioms employed in the reaction-pathway determination (Table 2-24).

Table 2-24 Sets of Axioms for Feasible Reaction Pathway and Combinatorially Feasible Reaction Networks, from Fan, et al. (2001)

Six axioms of feasible reaction pathways	Seven axioms of combinatorially feasible reaction networks
(R1) Every final product (target) is totally produced by reaction steps represented in the pathway. (R2) Every starting reactant (precursor) is totally consumed by reaction steps represented in the pathway. (R3) Every active intermediate produced by any reaction step represented in the pathway is totally consumed by one or more reaction steps in the pathway; and every active intermediate consumed by any reaction step represented in the pathway is totally produced by one or more reaction steps in the pathway. (R4) All reaction steps represented in the pathway are identified a priori. (R5) The network representing the pathway is acyclic. (R6) At least one elementary-reaction step represented in the pathway effects the activation of a starting reactant (precursor).	(T1) Every final product (target) is represented in the network. (T2) Every starting reactant (precursor) is represented in the network. (T3) Each reaction step represented in the network is defined a priori. (T4) Every active species represented in the network has at least one path leading to a final product (target) of the overall reaction. (T5) Every chemical or active species represented in the network must be a reactant for or a product from at least one reaction step represented in the network. (T6) A reactant of any elementary reaction represented in the reaction network is a starting reactant (precursor) if it is not produced by any reaction step represented in the network. (T7) The network includes at least either the forward or reverse step of each elementary reaction represented in the network.

P-graph is an unambiguous network representation in the reaction-pathway determination. P-graph is a bipartite graph. It is represented as (M, O) with the set of vertices $M \cup O$, and the set of arcs $\{(x, y) : y = (\alpha, \beta) \in O$ and $x \in \alpha\} \cup \{(y, x) : y = (\alpha, \beta) \in O$ and $x \in \beta\}$, where O is the set of elementary-reaction steps and M is the set of chemical or active species under consideration.

$O \subseteq P(M) \times P(M)$, where $O \cap M = \varnothing$. (α, β) is a reaction step if $(\alpha, \beta) \in O$, and α is called the input set and β the output set of this step. P-graph (M, O) representing a reaction network is combinatorially feasibel if it satisfies axioms (T1) through (T7) in Table 2-24. Also P-graph (M, O) representing a reaction pathway is feasible if it satisfies axioms (R1) through (R6) in Table 2-24.

There are several efficient algorithms come out from the axioms in Table 2-24 to carry out the synthesis of a feasible network of elementary reactions. Algorithm RPIMSG is for the maximal structure generation which contains all combinatorially feasible structures satisfying axioms (T1) through (T7) in Table 2-24, i.e. reaction networks or pathways. Algorithm RPISSG is for solution structure generation, which generates the set of all combinatorially feasible reaction networks from the maximal structure of reaction networks. Finally algorithm PBT is for feasible pathway generation, which ascertains if each combinatorially feasible reaction network or pathway is indeed a feasible pathway under axioms (R1) through (R5) in Table 2-24.

In summary, reaction path synthesis can well be solved using mathematical programming. The reaction pathway gives no information on the reaction rate, reversibility, equilibrium and reaction extent. So the final selection of valid reaction path must be determined by comparison of the rate expression derived from the feasible reaction pathways with the experimental data.

G. Summary

Sustainable development is about making choices and rendering actions that leave no unnecessary environmental strain for future generations. Sustainability calls for balancing the economic concerns with the environmental and social issues. Industrial ecosystem was first defined by describing the complex at Kalundborg, Denmark. The conclusion was that chemical complexes employing industrial ecology are more sustainable and profitable than the separate and independent plants (Ehrenfeld and Gertler, 1997). TCA and LCA were developed by the Constable, et al. (2000) for internal managerial decision-making. However, for both LCA and TCA the greatest obstacle is the availability of data for some materials and processes. Currently Type V cost (external cost, or sustainable cost) in TCA are not actually considered by Dow Chemical Company for lack of the data (Koch, 2001).

There were many methods and tools to measure the sustainability of products and processes. SPI was proposed to measure the total environmental impact of human activities of various kinds, and it used an ecological evaluation system for process engineering with the comparison of different systems and the various partial pressures from one system on the environment (Krotscheck and Narodoslawsky, 1996, 2001). The shortcoming of SPI is no consideration of social factors, regional restriction, and it is difficult to extend it to the global application. Similarly, environmental and economic factors were incorporated together without social factors by Chen and Shonnard (2001). Meanwhile, metrics and indicators for sustainable development were developed to measure the economic, environmental and social effects of the business triple bottom line. These metrics and indicators were not efficiently and reasonably incorporated together in the decision model. The external cost in power generation system has been studied for a long time but with a limited development and restricted only in power generation area.

Eco-efficiency emphasizes the relationship between producing and ecology system. Eco-efficiency is one part of sustainability, dealing with economic and environmental performance in the sustainability. Eco-efficiency metrics should be used together with social performance metrics to evaluate the sustainability of products or processes.

In order to have sustainable development, green chemistry and green engineering were described with the pollution control. Emission reduction, especially for emissions of greenhouse gases, was carried out with sustainable cost. There were many ways to estimate the sustainable cost, such as shadow price of carbon. Also there were several ways to achieve sustainable development, especially according to Kyoto Protocol there were emission-trading systems including carbon trading and nutrient trading. BEN is the EPA computer model to calculate the economic benefit of a pollution control violation.

Reaction path synthesis can be formulated as a mathematical programming pattern. The reaction pathway gives no information on the reaction rate, reversibility, equilibrium and reaction extent. So the final selection of valid reaction path must be determined by comparison of the rate expression derived from the feasible reaction pathways with the experimental data. Meanwhile, there is no consideration of total cost for the reactions.

In general, TCA, LCA, eco-efficiency and sustainability metrics can be used to evaluated new products and processes (Kohlbrand, 1998). Also, modeling technology can be used to describe and predict the performance of new processes in term of traditional variables of production, product quality and efficiency but also include environmental, health safety and sustainability evaluation. There is not enough standard methodologies and measurement developed in the past two decades (Kohlbrand, 1998). Some of these tools are available individually, such as TCA, LCA, and some other being developed, for example, metrics for sustainability. SPI can be employed to tell if one process is eco-efficient or not. Also, sustainability metrics can be used to compare different independent processes. Only recently can we evaluate the best configuration for processes based only on raw materials availability and products desirability. At this point in time, there is no integrated set of tools, methodology or programs to perform a consistent and accurate evaluation of new plants and existing processes.

No one has provided the method to evaluate the sustainable development of the chemical complex from macro-approach, which is the main task in this research. In the next chapter Chemical Complex Analysis System will be described which combines economic, environmental and sustainable costs basing on the TCA and incorporates EPA Pollution Index methodology (WAR) algorithm to get the best configuration of plants in a chemical complex effectively. The system will use a chemical production complex with thirteen multiple plant production units in the lower Mississippi River corridor, as base case. Thus, the base case is expanded to the superstructure with alternative ways to produce intermediates that reduce wastes and energy and consume greenhouse gases. The system will demonstrate the capabilities to select an optimum configuration of plants in a chemical production complex incorporating economic, environmental and sustainable costs, along with considering the energy saving and CO_2 reuse.

Reactions using greenhouse gases and nanotechnology that can produce potentially commercial products are to be determined. CO_2 reuse as a feedstock can lead to the reduction of CO_2 emission and alleviating global warming. The non-commercialized new/experimental processes will be designed with HYSYS to get the material and energy balances. All new plants will be integrated into the complex with using the Chemical Complex Analysis System. Meanwhile, the database of plants and flows among chemical plants and refineries will be developed.

In summary, our research develops an integrated system for use by plant and design engineers. They can convert their company's goals and capital into viable projects that meet economic, environmental and sustainable requirements on the base of meeting the triple bottom line for business.

CHPATER III METHODOLOGY OF CHEMICAL PRODUCTION COMPLEX OPTIMIZATION

A. Introduction

The business focus of chemical companies has moved from a regional to a global basis and this has redefined how these companies organize and view their activities. As described by H. J. Kohlbrand of Dow Chemical Company (Kohlbrand, 1998), the chemical industry has gone from end-of-pipe treatment to source reduction, recycling and reuse. There are great opportunities to reduce or eliminate waste, reduce environmental impacts of products and processes and create a sustainable future. Proper identification of real, long-term costs will result in the best list of prospects to compete for capital investment. This will require creative use of optimization technology using multiple objective functions for process synthesis. Process economics and environmental models are needed to define the optimum space for products and processes.

The domestic chemical industry is an integral part of the nations economy and consistently contributes a positive balance of trade. The industry consumes about 6.3 quads in energy feedstocks and energy from natural gas and petroleum to produce more than 70,000 diverse products (Pellegrino, 2000). Growth and productivity are coming under increased pressure due to inefficient power generation and greenhouse gas emission constraints.

A Chemical Complex Analysis System is being developed to assist in overcoming these limitations by developing and applying a regional methodology for conversion of greenhouse gases to saleable products. A prototype of the System has been completed, and it has been applied to a chemical production complex in the lower Mississippi River corridor. The Chemical Complex Analysis System will be used by corporate engineering groups for regional energy, economic, environmental and sustainable development. It will be applied to multi-plant chemical complexes to move to energy efficient and environmentally acceptable plants and to have new products from greenhouse gases. Using this integrated methodology, engineers will have a new capability to consider projects in depths significantly beyond current capabilities. They will be able to convert the company's goals and capital into viable projects that are profitable and meet economic, environmental and sustainable requirements. In addition, they have to perform evaluations for impacts associated with greenhouse gases and finite resources. This program is used with these projects, and these evaluations also demonstrate that plants are delivering energy efficient, societal and business benefits that will help ameliorate command and control regulations.

Each optimization problem in chemical production complex optimization has a similar mathematical statement as following:

Optimize: Objective function

Subject to: Constraints from plants model

where the objective function is a profit function (economic model) for complex economic optimization. The constraint equations describe the relationship among variables and parameters in the processes, and they are material and energy balances, chemical reaction rates, thermodynamic equilibrium relations, and others.

B. Methodology of Chemical Complex Analysis System

New methodology has been developed that determines the best configuration of plants in a chemical complex based on economic, energy, environmental and sustainable costs. The system structure is shown in Figure 3.1.

The Chemical Complex Analysis System incorporates a flowsheeting component as shown in Figure 3.1 where simulations of the plants in the complex are entered. Each simulation includes the process or block flow diagram with material and energy balances, rate equations, equilibrium relations and thermodynamic and transport properties for the process units and heat exchanger networks. These equations are entered through windows and stored in the database to be shared with the other components of the system.

The objective function is entered as an equation associated with each process with related information for prices and economic, energy, environmental and sustainable costs that are used in the evaluation of the Total Cost Assessment (TCA) for the complex. The TCA includes the total profit for the complex that is a function of the economic, energy, environmental and sustainable costs and income from sales of products. Then the information is provided to the mixed integer nonlinear programming solver to determine the optimum configuration of plants in the complex. Also, sources of pollutant generation are located by the Pollution Index component of the system using the EPA Pollution Index methodology (Cabezas, et al., 1997).

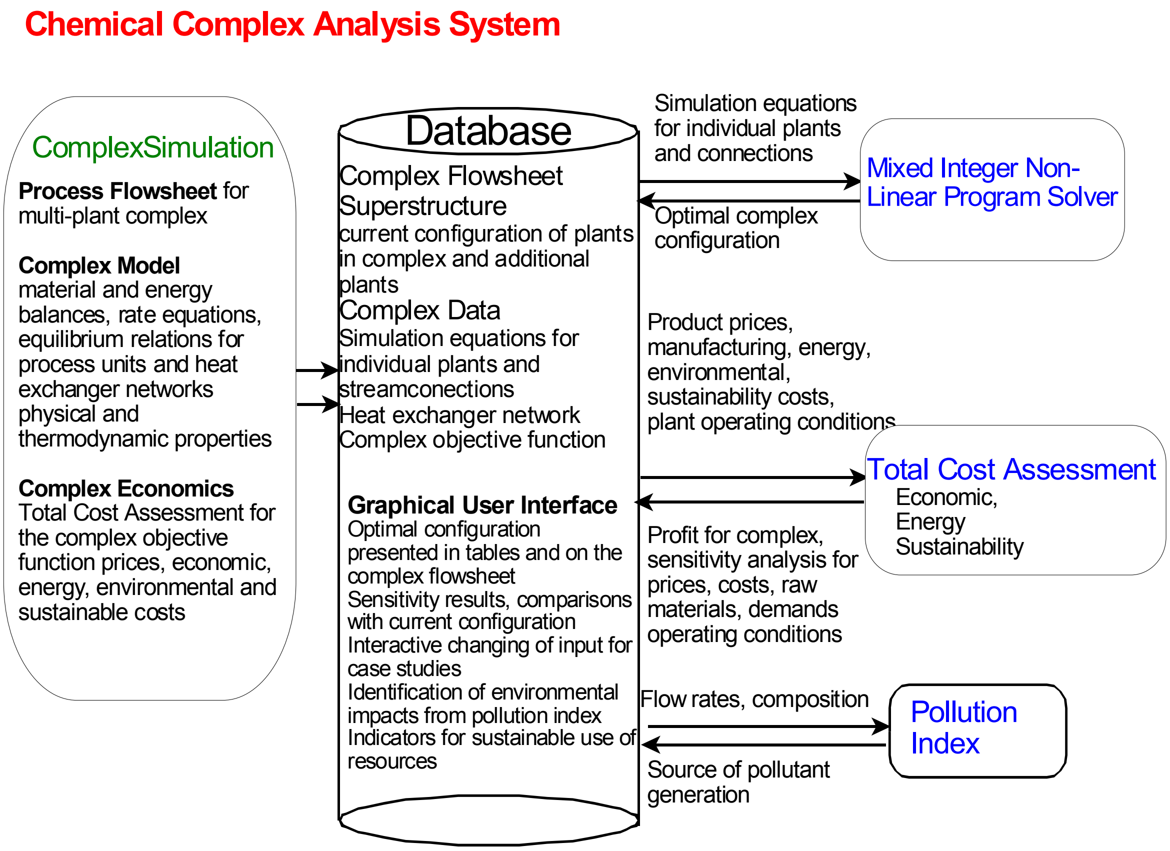


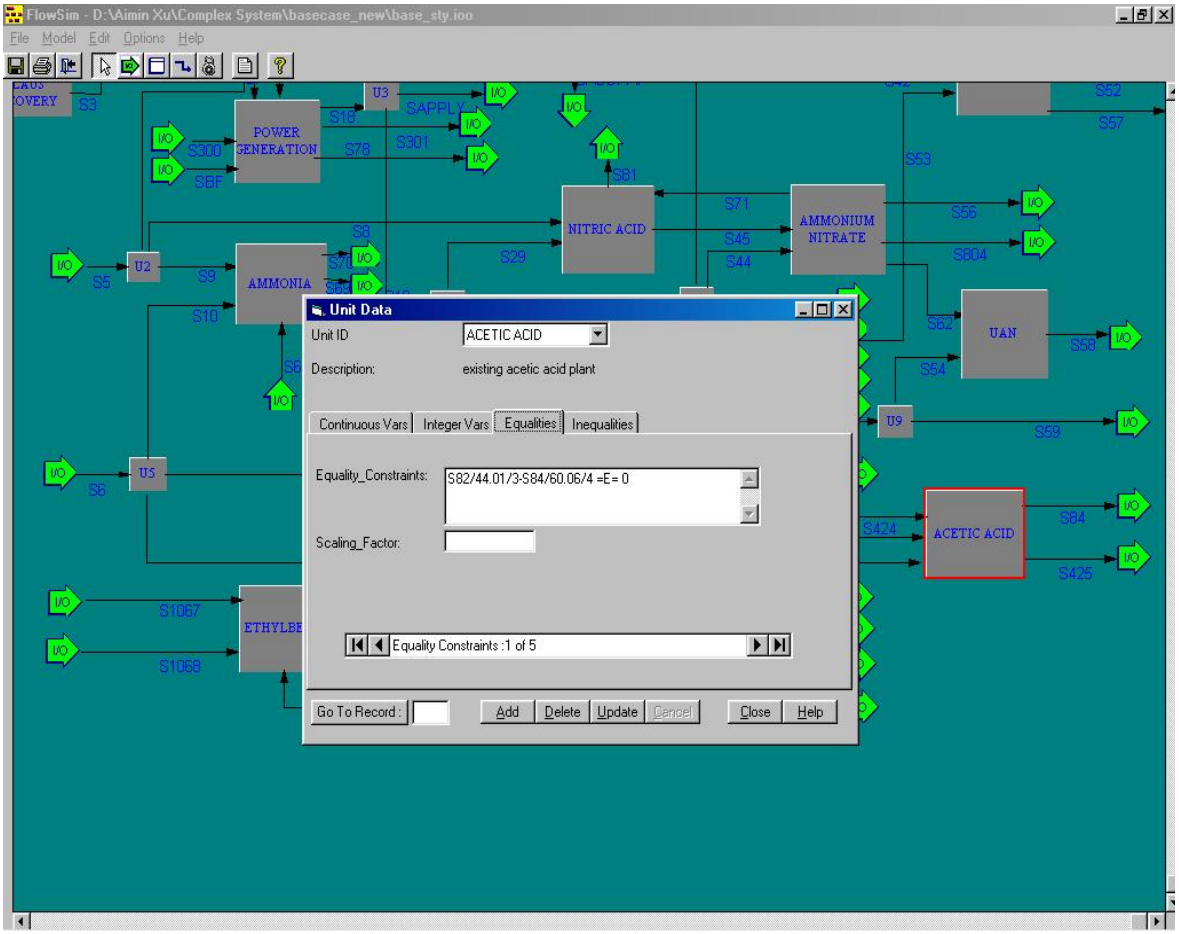
Figure 3.1 Program Structure for the Chemical Complex Analysis System

All interactions with the system are through a graphical user interface that is designed and implemented in Visual Basic. As shown in the diagram (Figure 3.1), the process flow diagram for the complex is constructed, and equations for the process units and variables for the streams connecting the process units are entered and stored in an Access database using interactive data forms as shown on the left side in Figure 3.1. Material and energy balances, rate equations and equilibrium relations for the plants are entered as equality constraints using the format of the GAMS programming language that is similar to Fortran and stored in the database. Process unit capacities, availability of raw materials and demand for product are entered as inequality constraints and stored in the database. The System takes the equations in the database and writes and runs a GAMS program to solve the mixed integer nonlinear programming problem for the optimum configuration of the complex. Then the important information from the GAMS solution is presented to the user in a convenient format, and the results can be exported to Excel, if desired. Features for developing flowsheets include adding, changing and deleting the equations that describe units and streams and their properties. Usual Windows features include cut, copy, paste, delete, print, zoom, reload, update and grid, among others. A typical window for entering process information is shown in Figure 3.2, and in this figure a material balance equation for the acetic acid process, ACETIC ACID, has been entered as an equality constraint. A detailed description of these operations will be provided in an interactive user's manual with help files and a tutorial.

The system has the TCA component prepare the assessment model for use with determination of the optimum complex configuration. Economic costs are estimated by standard methods (Garrett, 1989). Environmental costs are estimated from the data provided by Amoco, DuPont and Novartis in the AIChE/CWRT TCA report. Sustainable costs are estimated from the air pollution data in the AIChE/CWRT TCA report. Improving the estimates is an on-going effort.

In summary, the Chemical Complex Analysis System incorporates economic, energy, environmental and sustainable costs which provides the criteria for the best economic-environmental design; solves for the optimum configuration of plants;

incorporates EPA Pollution Index methodology; applied successfully to a chemical production complex; and developed by university-industry team.



Unit ID: ACETIC ACID

Description: existing acetic acid plant

Equality_Constraints: S82/44.01/3-S84/60.06/4 =E= 0

Scaling_Factor:

Equality Constraints :1 of 5

Figure 3.2 Illustration of Input to the System for Unit Data

C. Application to Plants in the Lower Mississippi River Corridor

A chemical production complex based on the plants in the lower Mississippi river corridor was developed with information provided by the cooperating companies and other published sources, as shown in Figure 3.3. This complex is representative of the current operations and practices in the chemical industry, and is called the base case of the existing plants. This base case complex was used as the starting point to

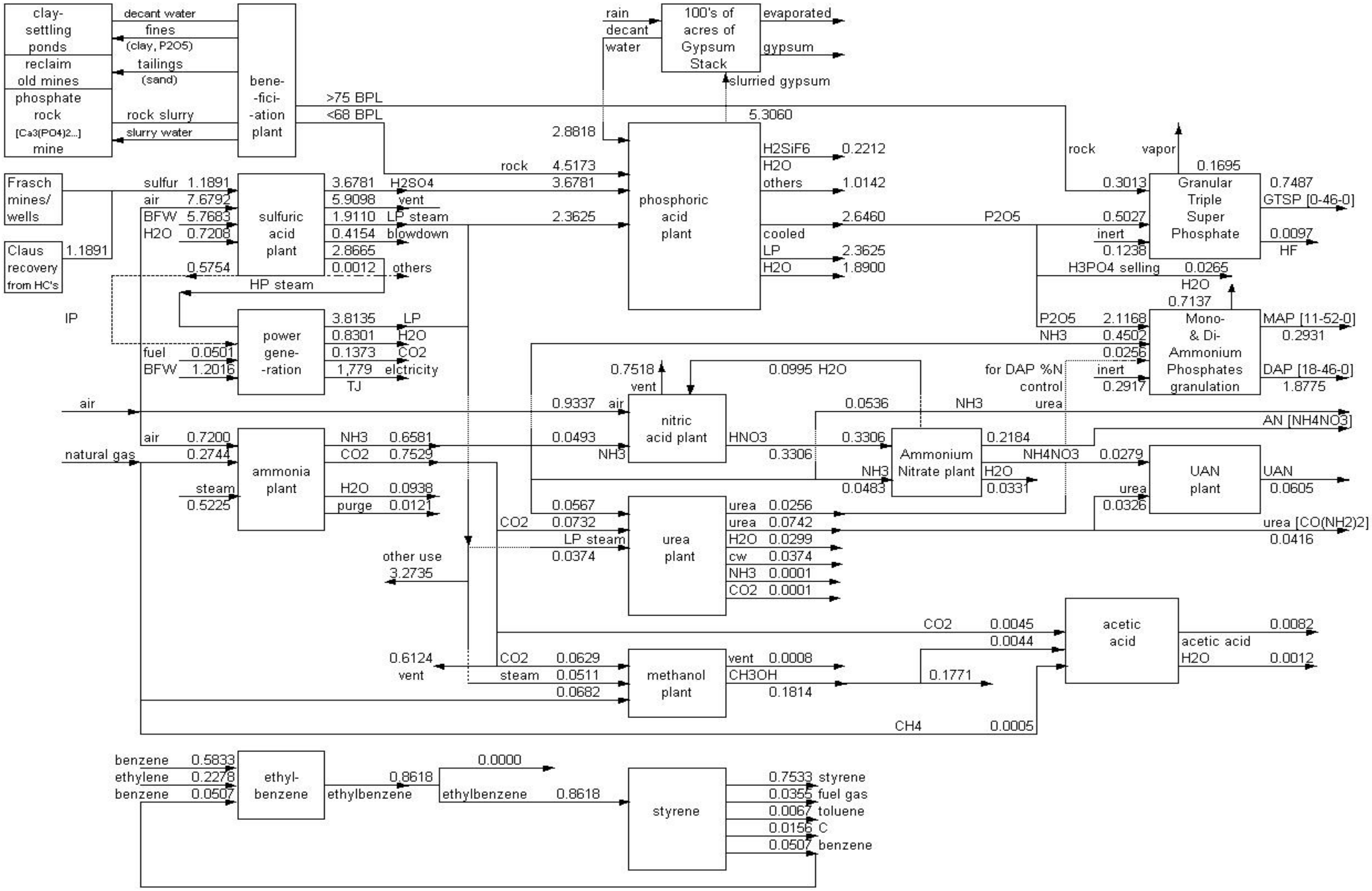


Figure 3.3 Chemical Production Complex in the Lower Mississippi River Corridor, Base Case, Flow Rates Million Metric Tons Per Year

develop a superstructure (Table 3-1) by adding plants, as shown in Figure 3.4. These additional plants gave alternate ways to produce intermediates, consume wastes and greenhouse gases and conserve energy. These additional plants could provide combinations leading to a complex with less environmental impacts and improved sustainability. Then this superstructure was evaluated to determine the optimum configuration using the economic, environmental and sustainable criteria in the System.

Table 3-1 Processes in Chemical Production Complex Base Case and Superstructure

Plants in the Base Case	Plants Added to Form the Superstructure
Ammonia	Methanol - Bonivardi, et al., 1998
Nitric acid	Methanol – Jun, et al., 1998
Ammonium nitrate	Methanol – Ushikoshi, et al., 1998
Urea	Methanol – Nerlov and Chorkendorff, 1999
UAN	Ethanol
Methanol	Dimethyl ether
Granular triple super phosphate (GTSP)	Formic acid
MAP and DAP	Acetic acid - new method
Contact process for sulfuric acid	Styrene - new method
Wet process for phosphoric acid	Methylamines
Acetic acid – conventional method	Graphite
Ethyl benzene	Hydrogen/Synthesis gas
Styrene	Propylene from CO_2
Power generation	Propylene from propane dehydrogenation
	Electric furnace process for phosphoric acid
	Haifa process for phosphoric acid
	SO_2 recovery from gypsum waste
	S and SO_2 recovery from gypsum waste

As shown in Figure 3.3 for base case there are thirteen production units plus associated utilities for power, steam and cooling water and facilities for waste treatment. The process selection was based on the availability and capacity of the plants in the lower Mississippi River corridor. A production unit contains more than

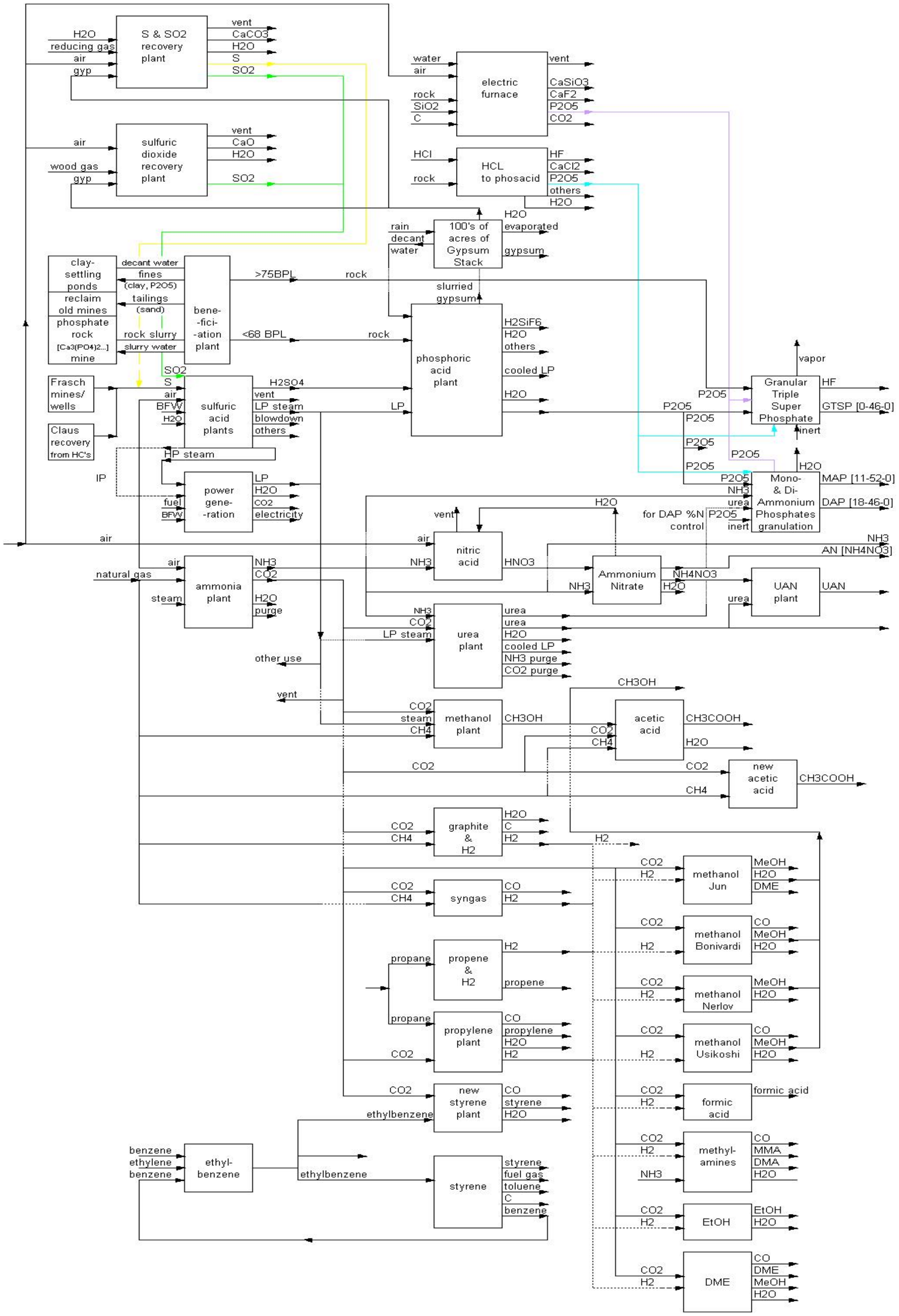


Figure 3.4 Chemical Production Complex in the Lower Mississippi River Corridor, Superstructure

one plant; and, for example, the phosphoric acid production unit contains four plants owned by three companies.

The raw materials used in the base case of the chemical production complex include air, water, natural gas, sulfur, phosphate rock, ethylene and benzene as shown on Figure 3.3. The products are mono- and di-ammonium phosphate (MAP and DAP), granular triple super phosphate (GTSP), urea, ammonium nitrate, and urea ammonium nitrate solution (UAN), phosphoric acid, ammonia, methanol, acetic acid, ethylbenzene and styrene. The flow rates shown on the diagram are in million metric tons per year. Intermediates are sulfuric acid, phosphoric acid, ammonia, nitric acid, urea, carbon dioxide and ethylbenzene. The intermediates are used to produce MAP and DAP, GTSP, urea, ammonium nitrate, acetic acid, UAN, and styrene. Ammonia is used in direct application to crops and other uses. MAP, DAP, UAN and GTSP are used in direct application to crops. Phosphoric acid can be used in other industrial applications. Methanol is used to produce formaldehyde, methyl esters, amines and solvents, among others, and is included for its use of ammonia plant byproduct - carbon dioxide. Acetic acid, ethylbenzene and styrene are used as feedstock in other chemical processes. Emissions from the chemical production complex include sulfur dioxide, nitrogen oxides, ammonia, methanol, silicon tetrafluoride, hydrogen fluoride and gypsum.

There were eighteen processes incorporated into the superstructure, among which fourteen processes were simulated with HYSYS for the new CO_2 consuming processes. These additional plants gave alternate ways to produce intermediates, consume wastes and greenhouse gases and conserve energy. More alternative and CO_2 used as feedstock processes were evaluated. The detailed information about the base case and superstructure will be discussed in the next chapter.

The System was used to obtain the optimum configuration of plants from the superstructure. The complete solution and a comparison of the base case and the optimal solution from the superstructure is given in Chapter V. These results illustrated the capability of the system to select an optimum configuration of plants in a chemical production complex and incorporate economic, environmental and sustainable costs.

D. Multiobjective Optimization

Multiobjective optimization, also called multicriteria optimization, is the simultaneous optimization of more than one objective function. The general Multiobjective Optimization Problem (MOP) can be formally defined as (Equation 3-1):

$$\begin{aligned} &\text{Minimize: } F(\mathbf{x}) = [f_1(\mathbf{x}), f_2(\mathbf{x}), \ldots, f_k(\mathbf{x})]^T \\ &\text{Subject to: } g_i(\mathbf{x}) \geq 0 \quad i = 1, 2, \ldots, m \\ &\qquad\qquad\quad h_j(\mathbf{x}) = 0 \quad j = 1, 2, \ldots, p \\ &\qquad\qquad\quad \mathbf{a} \leq \mathbf{x} \leq \mathbf{b} \end{aligned} \qquad (3\text{-}1)$$

Multicriteria optimization will be used to determine the optimal configuration of plants based on objective functions for economic, environmental and sustainable costs.

The feasible set is constrained by inequality and equality constraints and explicit variable boundaries, denoted as *C*. The definition of Pareto optimality is as followed (Coello, 2002). A point (a vector of decision variables) $\mathbf{x}^* \in C$ is said to be (globally) Pareto optimal for MOP (Equation 3-1) if and only if there is no $\mathbf{x} \in C$ such that $F_i(\mathbf{x}) \leq F_i(\mathbf{x}^*)$ for all $i = 1, \ldots, k$ with at least one strict inequality. Pareto optimal points are also known as efficient, non-inferior, or non-dominated points. A set of Pareto optimal points is called a Pareto optimal set. Pareto front is the plot of the objective functions whose non-dominated points are in the Pareto optimal set (Coello, 2002).

According to the influence of the decision maker (DM) in the optimization process, multiobjective optimization problem can be classified as no-preference, a priori, a posteriori and interactive methods (Table 3-2). In no-preference methods the multiobjective optimization problems are solved without the opinions of the DM. A priori methods are the methods where the DM must specify his preference before the solution process. A posteriori methods are the methods where the DM gives his preference after the solution process. In interactive methods the DM provides his opinions during the solution process. The more thorough discussion about some methods is as followed.

Both single and multiobjective optimization problems should be solved to get the global optimal solution. There are many approaches to carry the global optimization (Figure 3.5). These approaches were described in Coello (2002).

D-1. No-Preference Methods

In the non-preference methods, the opinions of the DM are not taken into consideration. These methods are suitable for situations where the DM does not have any special expectations of the solution and he is satisfied simply with some optimal solution (Miettinen, 1999). The two example no-preference methods are compromise programming and min-max formulation. These methods are described briefly below.

Table 3-2 A Classification of Multiobjective Optimization Methods, from Hwang, et al. (1980) and Mietten (1999)

Methods	Definition	Examples
No-preference methods	No articulation of preference information (Never)	• Compromising programming • Min-Max formulation
A priori methods	Priori aggregation of preference information (Before)	• Utility functions • Lexicographic ordering • Goal programming • Parametric approach • Non-linear combination • Fuzzy logic • Acceptability functions
Interactive methods	Progressive articulation of preference information (During)	• STEM method • Steuer method • Multiobjective Complex • Interactive surrogate worth trade-off method • Sequential proxy optimization technique • Reference point method
A posteriori methods	Posteriori articulation of preference information (After)	• ε-Constraint Method • Benson's method • Genetic Algorithms • Evolutionary Algorithms • Simulated Annealing • Normal boundary interaction • Weighted sum

D-1-1. Compromise programming

Compromise programming is also called the method of global criterion. Compromise solutions are the approximation of the ideal point (Equation 3-2). Ideal point can serve as a reference point, with the goal being seek for solutions as close as possible to the ideal point y^0. The following two mathematical expressions are equivalent. For the right one the L_p -metrics are used for measuring. There is only one solution for each choice of a norm, which is Pareto optimal (Ehrgott, 2000).

$$\begin{array}{l} min \quad d(f(x)-y^0) \\ x \in X \\ d(a,b) = \| a-b \| \\ d(a,b) = 0\, iff\ a=b \end{array} \quad \longrightarrow \quad \begin{array}{l} min \quad (\sum_{i=1}^{k} | f_{i(x)} - y_i^0 |^p)^{1/p} \\ subject\, to\, x \in X \\ 1 \le p < \infty \end{array} \tag{3-2}$$

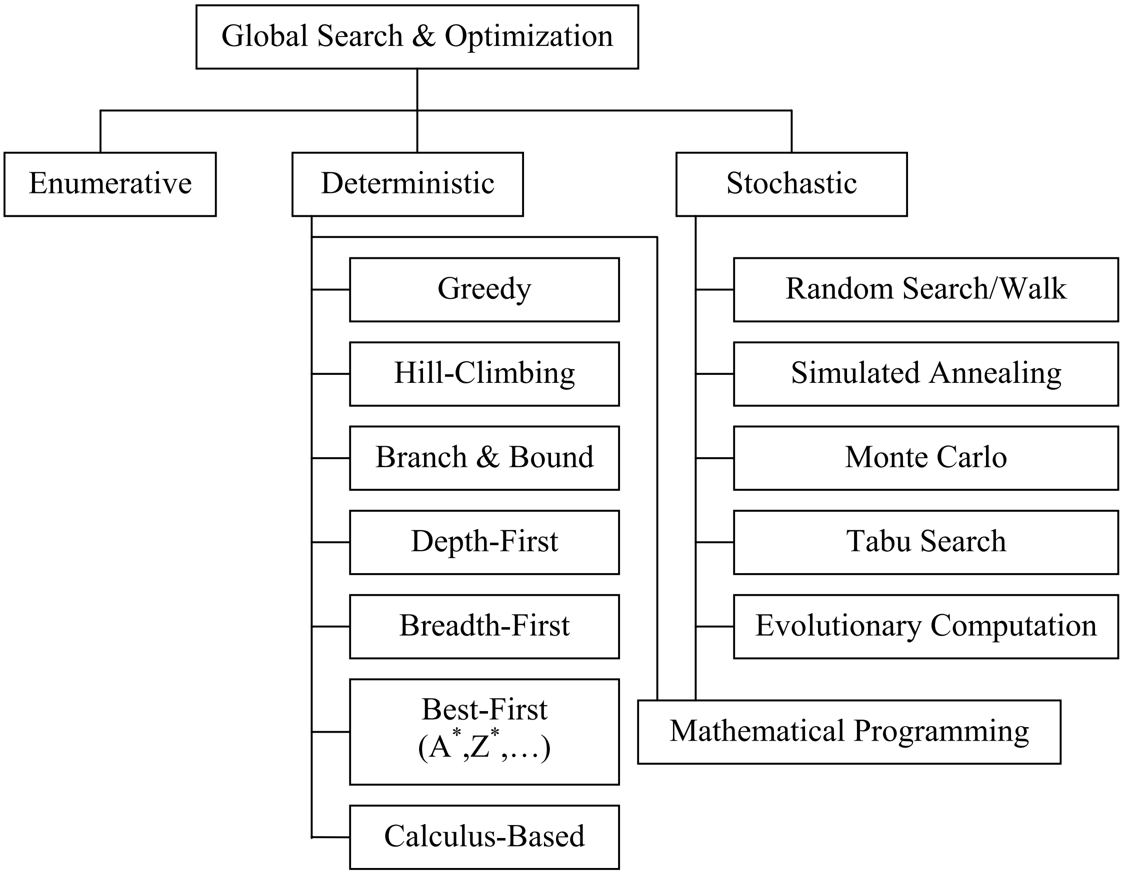


Figure 3.5 Global Optimization Approaches, from Coello (2002)

D-1-2. Min-Max Formulation

The objective is to minimize the relative deviations from the individual optimum of the single objective functions. It tries to minimize the objective conflicts

(Bhaskar, et al., 2000). Additional definitions are given by Bhaskar, et al. (2000) and Deb (2001).

D-2. A Priori Methods

In a priori methods, the DM must specify his preference and opinions before the solution process. These methods include utility functions, lexicographic ordering, goal programming, and parametric approach. These methods are described below, and all are used when the information about the preference of objectives is available.

D-2-1. Utility Functions

Utility functions are also called value function methods. The different objective functions $f_1(x), f_2(x), \ldots, f_n(x)$ can be expressed as a scalar utility function $U(f_1(x), f_2(x), \ldots, f_n(x))$. The utility is a way to describe the goals of the DM in an abstract way. The utility function can be solved by some method for single objective optimization. The drawback is that it is very difficult to determine the utility function (Bhaskar, et al., 2000).

D-2-2. Lexicographic Ordering

The DM is asked to rank the objectives in order of importance. The optimum solution is then obtained by minimizing the objective functions, starting with the most important one and proceeding according to the assigned order of importance of the objectives. If the problem has a unique solution after the most important objective function is solved, it is the solution of the whole multiobjective optimization problem. Otherwise, the second most important objective function is minimized with the addition of the new constraints from the most important objective to preserve its optimal value. It requires a pre-defined ordering of objectives and is inappropriate when there is a large number of objectives. The drawback is that the solution is very sensitive to the ranking of the objectives (Bhaskar, et al., 2000) and if the most important objective has the unique solution the other objectives do not have any influence on the solution (Miettinen, 1999).

D-2-3. Goal Programming

An objective $f_i(x)$ is reformulated into a goal by considering an aspiration level b_i. With the addition of slacks or deviations $s_i^+ \geq 0$ and $s_i^- \geq 0$, the goals can be achieved by minimize appropriate slacks (Table 3-3) (Ballestero and Romero, 1998).

Table 3-3 Goal Programming Formulation

Goal type	Goal programming form	Slacks to be minimized
$f_i(x) \leq b_i$	$f_i(x) - (s_i^+ - s_i^-) = b_i$	s_i^+
$f_i(x) \geq b_i$	$f_i(x) - (s_i^+ - s_i^-) = b_i$	s_i^-
$f_i(x)=b_i$	$f_i(x) - (s_i^+ - s_i^-) = b_i$	$s_i^+ + s_i^-$

Non-preemptive goal programming is defined when the problem is modeled by using weights on the deviations to construct a single objective. Preemptive goal programming assumes a strict dominance order of the goals, which can be solved using a sequence of linear programming problems (sequential linear goal programming).

Coello (2002) classified goal programming as one of the target-vector approaches including goal programming, goal attainment and mix-max method, which defines a set of goals (or targets) that need to be achieved for each objective function and then minimize differences between the current solution and these goals. The disadvantage of the target-vector approach is difficult definition of goals.

D-2-4. Parametric Approach

Parametric approach is also called aggregating approach or weighted sum (Bhaskar, et al., 2000). It combines all the objectives into a single one using addition, multiplication or any other combination of arithmetical operations. Most important is weighted sum scalarization, min $\sum_{i=1}^{k} w_i f_i(x)$, where $\sum_{i=1}^{k} w_i = 1$, $w_i \geq 0$, are the weighting coefficients representing the relative importance of the *k* objective functions of the problem. In other words, the DM has to assign the relative weights to each of the objective functions according to their relative importance. In order to produce desirable solutions in proportion to the ranges of the objective functions, the objective functions should be normalized or scaled to get approximately same magnitude of their objective values.

The parametric approach can be used without the weighting coefficient information from the DM. In this case, it is a posteriori methods. When the problem is not convex or with duality-gaps, it can not generate the entire Pareto optimal set (Pareto front) (Bhaskar, et al., 2000).

D-3. A Posteriori Methods

A posteriori methods could also be called methods for generating Pareto optimal solutions (Miettinen, 1999). These methods include ε-constraint method, Benson’s method, genetic algorithms and evolutionary algorithms, and simulated annealing. These methods are described below, and all are used when there are no preferences of the objectives from the DM and a Pareto optimal set is required.

D-3-1. ε-Constraint Method

$$\begin{aligned} &\min \quad f_l(x) \\ &\text{subject to } f_j(x) \le \varepsilon_j \text{ for all } j = 1, \dots, k, j \ne l, l \in \{1, \dots, k\} \end{aligned} \tag{3-3}$$

This method minimizes the most preferred or primary objective function, and considers the other objectives as constraints bound by some allowable levels ε_I (Equation 3-3) (Miettinen, 1999). The levels ε_i are altered to generate the entire Pareto optimal set. It is easy to implement but with potentially high computational cost. Three different adaptations are available: the equality constraint approach, the inequality constraint approach and the hybrid (weighting-constraint) approach. The third type combines the principles of the aggregating approach with the ε-constraint technique. Although this technique can be used to solve non-convex problems, the difficulty is that an “a-priori” knowledge of the appropriate range of values of ε_i is required (Bhaskar, et al., 2000).

D-3-2. Benson’s method

For $\min(f_1(x), \dots, f_Q(x))$, define $\varepsilon_i = f_i(x^0) - f_i(x)$, where x^0 is the initial feasible solution and ε_i are nonnegative deviation variables, then the new optimization problem is generated as Equation 3-4 (Ehrgott, 2000). To obtain different Pareto optimal solutions, the differences ε_i can be weighted before summation. Hence, by changing the weight factor, different Pareto points can be obtained (Deb, 2001).

$$\begin{aligned}&\max\sum_{i=1}^{Q}\varepsilon_i\\&f_i(x^0)-\varepsilon_i-f_i(x)=0\qquad\qquad(3\text{-}4)\\&\varepsilon_i\geq 0, x\in X\end{aligned}$$

Note that all of above methods for multiobjective optimization problems replace a multiobjective problem by a single objective problem. However, the following approaches do not.

D-3-3. Genetic Algorithms and Evolutionary Algorithms

Genetic algorithms and the closely related evolutionary algorithms (also called advanced form of genetic algorithms) are a class of nongradient methods which has grown in popularity ever since Rechenberg (1973) and Holland (1975) first published their work. Both genetic and evolutionary algorithms simulate natural genetic processes of living organisms, and they can often outperform conventional optimization methods when applied to difficult design optimization problems. Since it is difficult to draw a line between a genetic algorithm and an evolutionary algorithm, these terms have been used interchangeably.

Genetic algorithms mimic the process of natural selection and natural genetics. Each optimization variable is encoded by a gene with an appropriate representation, such as a real number or a string of bits. The corresponding genes for all variables comprise a chromosome with its fitness value assigned by the model, which can describe an individual design solution. A set of chromosomes forms a population or pool, where Darwinian principle of “survival of the fittest” is used to generate a new and improved population. This can be done by mating performed using crossover to combine genes from different parents to produce children, which is similar to those in genetic reproduction. The children are inserted to the pool and the gene pool evolves with the fitness improving over the generation.

Coello (2002) classified the genetic and evolutionary algorithms with the comparison in Table 3-4. Bhaskar, et al. (2000) predicted that in the future evolutionary algorithms become more popular because they are quite robust for generating non-inferior solutions for large-scale complex problems. For more complex problems where the constraints are not known in a very precise manner, two Pareto sets are needed to decide the preferred solutions. One is between the objective functions, and the other is between the extents of constraints-violation.

D-3-4. Simulated Annealing

Meanwhile, another non-traditional algorithm is simulated annealing (SA) (Kirpatric, et al., 1983; Aarts and Korst, 1989). It mimics the cooling of molten metals. Working with a single point each time, the new point is created at each iteration according to the Boltzmann probability distribution. Deb (1995) reported that it was effective in finding global optimum solutions when a slow cooling procedure is used.

D-4. Interactive Methods

This class of interactive methods is the most advanced of the four classes of the methods for the multiobjective optimization (Miettinen, 1999). The assumption for this class is the full cooperation of the DM to get the most satisfactory results. The advantages of these methods are: only part of the Pareto optimal points have to be generated and evaluated; the DM can specify and update his preference during the solution process as he gets to the problem and its potentialities; and the DM can have more confidence in the final solution because he is involved throughout the solution process. More information can be obtained from Miettinen (1999).

Table 3-4 Classification of Genetic and Evolutionary Algorithms, from Coello (2002)

Name	Comments
First generation techniques	
Non-Pareto approaches:	No incorporation of Pareto optimum concept.
• Vector evaluated genetic algorithm (VEGA)	• Use subpopulations to optimize each objective separately. Not necessarily produce nondominated vectors.
Pareto approaches:	Use of nondominated ranking and selection to move the population towards the Pareto front. Require a ranking procedure and a technique to maintain diversity in the population.
• Multi-objective genetic algorithm (MOGA)	• The rank of a certain individual corresponds to the number of individuals in the current population by which it is dominated. Use fitness sharing and mating restrictions. Its performance depends on the appropriate selection of the sharing factor.
• Nondominated sorting genetic algorithm (NSGA)	• Nondominated individuals get a certain dummy fitness value and then are removed from the population. Defect is very sensitive to the value of the sharing factor.
• Niched-Pareto Genetic Algorithm (NPGA)	• Use a tournament selection scheme based on Pareto dominance without Pareto ranking. Requiring a sharing factor, also another factor-tournament size.
• NPGA2	• Uses Pareto ranking but keeps tournament selection.
Second generation techniques	Nondominated and uniformly distributed solutions
• The Pareto archived evolution strategies (PAES)	• (1+1) evolution strategy with adaptive grid
• The Pareto envelop-based selection algorithm (PESA)	• Small internal and large external population, hyper-grid
• PESA-II	• Region-based selection is adopted based on PESA

Table 3-4 Continued

Second generation techniques (Continued)	Nondominated and uniformly distributed solutions (Continued)
• The strength Pareto evolutionary algorithm (SPEA)	• Strength value, a clustering technique-average linkage method
• SPEA2	• Based on SPEA, a fine-grained fitness assignment strategy, a nearest neighbor density estimation technique, and an enhanced archive truncation method.
• NSGA-II	• Uses elitism and a crowded comparison operator that keeps diversity without specifying any additional parameters.
• The multi-objective messy genetic algorithm (MOMGA)	• Extension of messy GA, three phases: initialization phase, primordial phase and juxtapositional phase.
• MOMGA-II	• Three phases: initialization phase, building block filtering phase, juxtapositional phase.
• Micro genetic algorithm (Micro-GA)	• Micro-GA cycle

D-5. Application of Multiobjective Optimization in the System

The above classifications for the multiobjective optimization are based on the influence of the DM in the optimization process. Non-preference methods are suitable for situations where the DM does not have any special expectations of the solution and he is satisfied simply with some optimal solution (Miettinen, 1999). A priori methods are suitable when the DM must specify his preference and opinions before the solution process. A posteriori methods are used when there are no preferences of the objectives from the DM and a Pareto optimal set is required. Interactive methods are the most advanced of the four classes of the methods for the multiobjective optimization, which need is the full cooperation of the DM to get the most satisfactory results (Miettinen, 1999).

For the chemical production complex multiobjective optimization, no preferences were provided and the ranges of the multiple objectives were unknown. Also, GAMS was used for optimization in the Chemical Complex Analysis System, and evolutionary algorithms and simulated annealing were not available as solvers. Consequently, parametric approach method was used for the multiobjective optimization. With this method, the relationships among the economic, environmental and sustainable costs were evaluated using the triple bottom line for the chemical production complex.

E. Monte Carlo Simulation

Monte Carlo methods, also known as Monte Carlo simulation or static simulation, are statistical simulation methods using sequences of random numbers to perform simulation. It is a general approach rather than a specific algorithm. The name "Monte Carlo" was coined by Metropolis inspired by Ulam's interest in poker during the Manhattan Project of World War II for the similarity of statistical simulation to games of chance, and also because the capital of Monaco was a center for gambling and similar pursuits. Monte Carlo simulation will be used to determine the sensitivity of the optimal configuration of plants to price and cost parameters used in the optimization.

E-1. Introduction to Monte Carlo Simulation

The essential characteristic of Monte Carlo is the use of random sampling techniques with other possible algebra manipulating the outcomes to arrive at a solution of the physical problem. The major components of a Monte Carlo methods or algorithm are described by Computational Science Education Project (1995a) (Table 3-5).

The sequence of random numbers generated by the random generator in a Monte Carlo simulation should have the following four properties (Computational Science Education Project, 1995b):

- Uncorrelated sequences: any subsequence of random numbers should not be correlated with any other subsequence of random numbers. N-tuples of random numbers should be independent of each other.
- Long period: the repetition should occur only after a very large set of random numbers has been generated.
- Uniformity: the random number sequence should be unbiased and uniform, which means equal fraction of random numbers should fall into equal "area" in space.
- Efficiency: the random number generator should be efficient.

Table 3-5 Major Components of a Monte Carlo Algorithm, from Computational Science Education Project (1995a)

Component Name	Description
Probability Distribution Functions (PDF)	To describe the physical or mathematical system.
Random number generator	To generate random numbers uniformly distributed on the unit interval.
Sampling rule	To formulate sampling from the specified PDF.
Scoring (Tallying)	To accumulate the outcomes into overall tallies or scores for the quantities of interest.
Error estimation	To estimate the statistical error (variance) and mean as a function of the number of samples.
Variance reduction techniques	To reduce the variance in the estimated solution to reduce the computational time.
Parallelization and vectorization	To implement Monte Carlo methods on advanced computer architectures.

For the mode with n uncertain parameters, the uncertain input domain of sampling points is the *n*-dimensional space. In crude Monte Carlo simulation, a value is drawn at random from the specified distribution for each input parameter. A scenario is defined as the set of the random values drawn for all of the n parameters, which is used as input to generate the corresponding output value. The entire process is repeated *m* times to produce *m* independent scenarios with the corresponding output values. These *m* output values constitute a random sample from the probability distribution over the output induced by the probability distribution over the inputs. Hence, the precision of the output distribution can be estimated from this sample of output values using standard statistical techniques. The effort to run the model for each scenario is typically proportional to the number of uncertain inputs *n*, which means the computational complexity of Monte Carlo sampling is linear in *n*. The number of runs, *m*, is determined only by the relative accuracy required for the output distribution, not by the number of uncertain inputs *n*, for a given degree of uncertainty.

Classical Monte Carlo simulation usually assumes a probability distribution a priori. Lagoa and Barmish (2001) provided a new theory, distributionally robust Monte Carlo simulation, which does not need the input of parameter probability distributions. Instead of using some rather arbitrary probability distribution a priori, they considered distributional robustness to find the appropriate distribution a posterior to use. They typically started only with bounds on the uncertain parameters without the probability distribution assumption. But their work was only for the parameters, and the incorporation of design variables was their future work.

E-2. General Applications of Monte Carlo Simulation

Monte Carlo methods can be applied in many fields, such as stellar evolution, nuclear reactor design, radiation cancer therapy, quantum chromodynamics, oil well exploration, Dow-Jones forecasting, econometrics, and traffic flow. Generally, two standard applications are integration and optimization, which will be discussed below in detail.

Monte Carlo simulation can be used to evaluate an integral (Ecker and Kupferschmid, 1988). For example, $I(a,b)=\int_a^b f(x)dx$. A graph of the integrand function $f(x)$ with the area corresponding $I(a,b)$ shaded is provided. A rectangular box containing the entire area corresponding to the value of the integral can be selected, with the interval on the *x*-axis between the lower and upper limits of integration as its base. Using Monte Carlo simulation to generate points (x,y) randomly located within the box, check each point to see if it is above or below the graph of the integrand function and estimate the shaded area fraction from Equation 3-5. Then the integral value is total box area multiplied by the area fraction. The above is only a simple example for illustration. Usually, Monte Carlo simulation is used to evaluate the definite integration over several dimensions, such as nuclear physics.

$$\text{area fraction} \approx \frac{\text{number of random points } (x,y) \text{ having } y < f(x)}{\text{total number of random points tried}} \qquad (3\text{-}5)$$

Based on the Metropolis algorithm in 1953 for simulating a collection of atoms in thermal equilibrium at a given temperature, S. Kirkpatrick provided the process called optimization by simulated annealing for the travelling salesman problem, which is a specific example for the Monte Carlo simulation use in the optimization. In addition, Monte Carlo methods can be used in integer programs and evaluation of the mathematical programming algorithms and other numerical methods (Ecker and Kupferschmid, 1988).

E-3. Methods for Selection of Sample Size (Number of Monte Carlo Runs)

Basically, there are two methods to determine the sample size or runs of Monte Carlo simulation. One is selection of the sample size according to the uncertainty about the mean; the other is selection of sample size from estimating confidence intervals for fractiles.

E-3-1. Selection of the Sample Size According to the Uncertainty about the Mean

Assume a random sample of *m* output values generated by Monte Carlo simulation $(y_1, y_2, \cdots, y_m)$ (Equation 3-6 and 3-7).

$$\text{Mean: } \bar{y} = \frac{1}{m}\sum_{i=1}^{m} y_i \tag{3-6}$$

$$\text{Variance: } s^2 = \frac{1}{m-1}\sum_{i=1}^{m}(y_i - \bar{y}) \tag{3-7}$$

Given that confidence interval with confidence α, $(\bar{y} - c\frac{s}{\sqrt{m}}, \bar{y} + c\frac{s}{\sqrt{m}})$, where *c* is the deviation for the unit normal enclosing probability α. Since the two quantities enclosing the interval are random variables, i.e. the functions of the fixed but unknown mean and variance, the interpretation of the interval is that they have an α probability of enclosing the mean.

To get an estimate of the mean of y with a α confidence interval smaller than w units wide, the width of the interval must be less than w, i.e., $2c\frac{s}{\sqrt{m}} < w$; then get $m > \left(\frac{2cs}{w}\right)^2$.

The procedure of this method is: first make small Monte Carlo run with to get an initial estimate s^2, 20 output values, for example; then, use $m > \left(\frac{2cs}{w}\right)^2$ to estimate the number of samples needed in total to reduce the confidence interval to the presumed width w (Morgan and Henrion, 1990).

E-3-2. Selection of Sample Size from Estimating Confidence Intervals for Fractiles

The p fractile, Xp, of a distribution is a value such that there is a probability p that the actual value of the random variable will be less than that value, $P[X \le X_p] \equiv p$. If the probability is expressed in percent, the fractile value is referred to as a percentile. The pth percentile is defined to be that value of a variable for which p percent of the values of the distribution are smaller.

The following is the procedure for the sample size determination from estimating the confidence interval for fractiles (Morgan and Henrion, 1990).

Assume the values of y with sample size m. Relabel the values of y to be in increasing order, $y_1 \le y_2 \le \cdots \le y_m$. Sample y_i is an estimate of fractile Y_p, where $p=i/m$. The probability that exactly j of m values of y are not larger than fractile Y_p is $\binom{m}{j} p^j (1-p)^{m-j}$, where $\binom{m}{j} = \frac{m!}{j!(m-j)!}$. Generally speaking, the number j_p of sample values less than X_p has a binomial distribution with parameter p and m. The probability for two order statistics y_i, y_k, where $y_i<y_k$, to enclose fractile X_p is $P[x_i \leq X_p \leq x_k] = \sum_{j=1}^{k} \binom{m}{j} p^j (1-p)^{m-j}$. This can be evaluated with standard binomial distribution tables to obtain confidence interval for X_p.

If the number, j_p, of sample values not larger than Xp is reasonably large, the above binomial distribution can be approximated with a normal distribution with mean mp and variance $\sigma^2 = mp(1-p)$. Assume c is the deviation of the confidence interval for confidence α with unit normal distribution of random variable x, $P[-c \leq x \leq c] = \alpha$. The interval with confidence of α containing j_p is approximately $(mp - c\sigma, mp + c\sigma)$. Then, the number of ordered sample values in this interval is $2c\sigma = 2c\sqrt{mp(1-p)}$.

The uncertainty in the value of the fractile is determined by the particular values of the sample over the interval (i,k) defined as followed.

$$\begin{aligned} i &= \left\lfloor mp - c\sqrt{mp(1-p)} \right\rfloor \\ k &= \left\lceil mp + c\sqrt{mp(1-p)} \right\rceil \end{aligned} \tag{3-8}$$

The notation $\lfloor\ \rfloor$ and $\lceil\ \rceil$ are for rounding down and up respectively to the nearest integer. Hence, the approximate confidence interval with confidence α for fractile Y_p is (y_i, y_k).

For more precision, α confidence of Y_p should be between the sample values used as estimates of the p-Δpth and p+Δpth fractiles. The sample size should be obtained through the following procedure.

$$i = m(p - \Delta p)\,,\ k = m(p + \Delta p) \tag{3-9}$$

$$k - i = 2m\Delta p \tag{3-10}$$

Ignoring the rounding from Equation 3-8, $k - i = 2c\sqrt{mp(1-p)}$ (3-11)

So, $2m\Delta p = 2c\sqrt{mp(1-p)}$ (3-12)

The sample size is $m = p(1-p)(\frac{c}{\Delta p})^2$. (3-13)

E-4. Application of Monte Carlo Simulation in the System

Monte Carlo simulation is used in the Chemical Complex Analysis System for sensitivity analysis. First, distribution selection and evaluation, and correlation assumptions are described. Then, the sample size or runs of Monte Carlo simulation will be determined by the uncertainty about the mean and estimating confidence intervals for fractiles, respectively. According to the input parameter distributions to the model, the sensitivity analysis for economic, environmental and sustainable costs will be provided with distributions evaluated. Meanwhile, the selection of different processes in the chemical complex will also be discussed in the sensitivity analysis in the following chapters.

F. Pollution Index Program

The pollution assessment program measures the pollution impacts of chemical processes on the environment. The potential environmental impacts are calculated from stream mass flow rates, stream composition, and a relative potential environmental impact score for each chemical present. The Pollution Index program is used to identify streams and parts of chemical processes to be modified. Also, it allows comparison of pollution production of different chemical processes.

The pollution assessment module of Chemical Complex Analysis System is called Pollution Index program which determines the emissions from the process and the location where these pollutants are generated within the process. It is based on the WAste Reduction (WAR) algorithm and the Environmental Impact Theory as described by Telang (1998). It defines a group of quantities called as the Pollution Indices to provide a basis for measuring the pollution generated by the process.

First, in the Pollution Index program, this selection of input-output streams is automatically done based on the plant information entered in Flowsheet Simulation. Since environmental impact of a chemical process is caused by the streams that the process takes from and emits to the environment, only these input and output streams are considered in performing Pollution Index analysis. Other streams, which are completely internal to the process, are excluded.

The second step in the Pollution Index program is the classification of output streams into product and non-product streams. All streams either sold as product or used up in a subsequent process in the production facility are considered as product streams. All other output streams, which are released into the environment, are considered as nonproduct streams. All nonproduct streams are considered as pollutant streams whereas all product streams are considered to have no environmental impact.

In the third step, since Pollution Index of a stream is a function of its composition, the composition data for the stream is retrieved from the results of Complex Optimization performed earlier. This can be either in terms of mass flow rates or fractions. Also the specific environmental impact potential values of individual chemical species present in a stream are needed, which can be found in Heijungs, et al. (1992). Meanwhile, the relative weighting factors for the process plant are required for the nine category environmental impacts. The relative weighting factors allow the customization of the analysis to specific or local conditions. Their values depend on the location of the plant and its surrounding conditions. For example, the weighting factor for photochemical oxidation is larger than those of other impact in the area which suffers from smog.

In the final step the Pollution Index program is called to perform the analysis. Mass balance constraints are solved for the process streams involved, and equations of the Environmental Impact Theory are used to calculate the Pollution Index values. Six types of pollution indices are reported for the process. Three of these are based on internal environmental efficiency whereas the other three are based on external environmental efficiency. On the other hand, Pollution Indices for each of the individual process stream are calculated. These values help in identifying the streams which contribute more to the overall pollution impact of the process, so that suitable process modifications can then be done to reduce the pollutant content of these streams.

Every run of chemical complex optimization can be followed by Pollution Index calculations. The new Pollution Index values are compared with the older values. The comparison shows how the changes in process conditions affect the environmental impact. Thus, the Pollution Index program can be used in the continuous monitoring of the complex.

G. Summary

In summary, the Chemical Complex Analysis System (the System) can be applied to the chemical complexes in the world for the total cost assessment. Multiobjective optimization is used to analyze the relationships among the economic, environmental and sustainable costs in a chemical complex, especially for the impacts of sustainable costs. Monte Carlo simulation is employed for the sensitivity analysis of the chemical complex. Finally, the Pollution Index program is called for the pollution analysis to measure the environmental impact of the processes and to direct changes for waste reduction.

This chapter included the methodology of the Chemical Complex Analysis System. The subsequent chapters show the results of the System application. A base case of existing plants in the lower Mississippi River corridor is used to demenstrate the capabilities of the System.

CHAPTER IV PLANT MODEL FORMULATION

The methodology and procedure to use the Chemical Complex Analysis System has been outlined in previous chapter. This chapter deals with the development of process simulation and optimization model for the chemical production complex in the lower Mississippi River corridor. This complex is ideally suited for demonstration of the system performance. A detailed description of the complex is given below.

A. Chemical Production Complex

A-1. Introduction to the Chemical Production Complex

As the world economy develops, it is good for chemical industry to incorporate all possible production units to make the maximum profit. A chemical production complex was assembled with production units in the lower Mississippi River corridor (Figure 4.1) as shown in Figure 3.3. This was done with information provided by the cooperating companies and other published sources. This complex is representative of the current operations and practices in the chemical industry and was used as the base case and starting point to develop a superstructure (Figure 3.4) by adding plants. These additional plants gave alternate ways to produce intermediates that reduce and consume wastes and greenhouse gases and conserved energy. These additional plants could provide combinations leading to a complex with lower environmental impacts and greater sustainability. This superstructure was evaluated using the economic, environmental and sustainable criteria in the Chemical Complex Analysis System to obtain the optimum configuration.

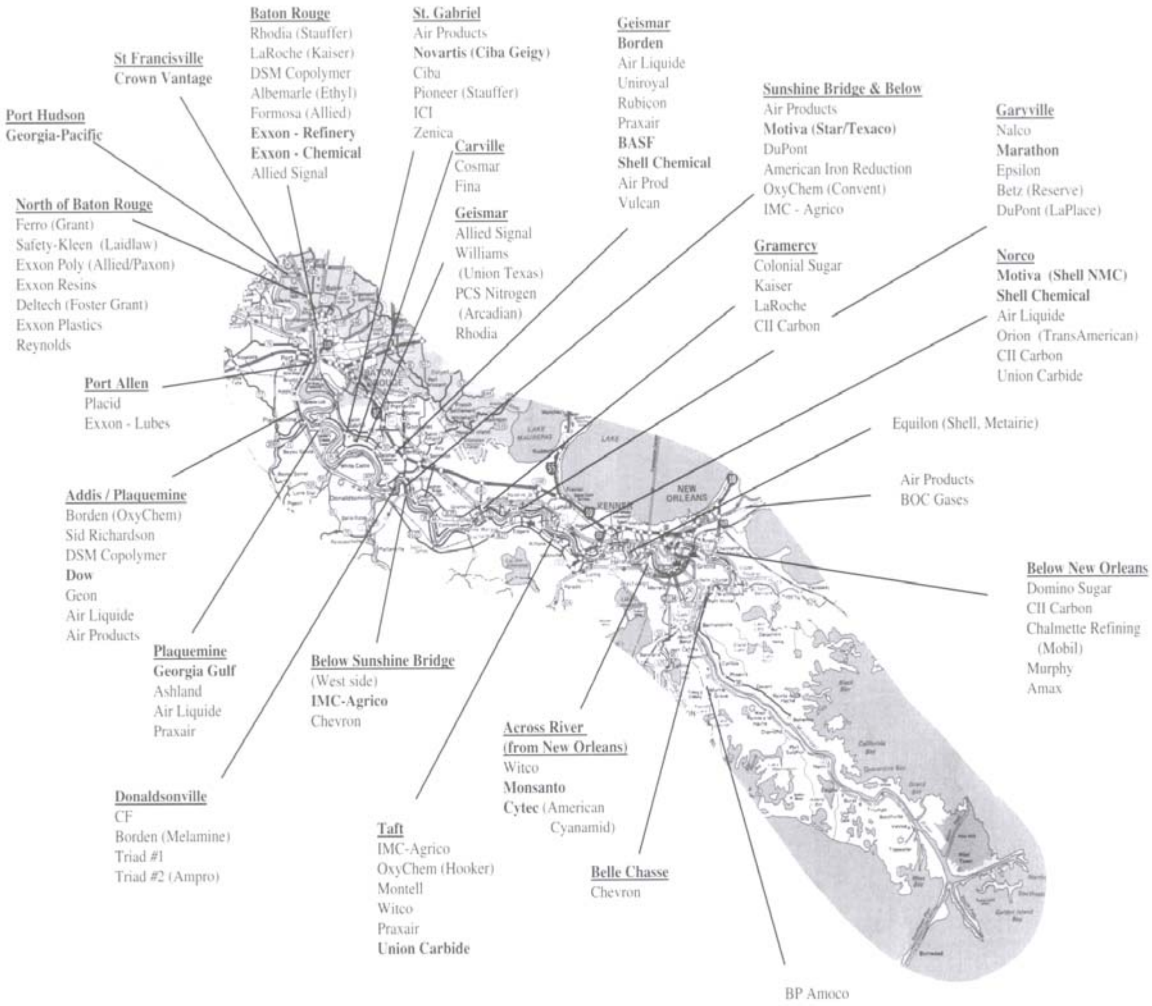


Figure 4.1 Chemical Plants along the Lower Mississippi River Corridor, from Peterson (2000)

The process simulation of each unit in the chemical production complex is given in the following section, along with how these plants are connected. First the process models for the plants in the base case will be given. The base case of existing plants was developed under the direction of the industrial advisory group. Then the process models for the additional plants added to form the superstructure will be given.

A-2. Process Models in the Chemical Production Complex

The model (simulation) of a process includes material and energy balances, rate equations and equilibrium relations. The material balance and energy balance equations for a process are given in a table. For each process this includes the overall mass balance and the component or species mass balances. The mass balance for each component is established based on the conservation law. The steady state mass balance for a component is written as:

$$F_{in}^{(i)} - F_{out}^{(i)} + F_{gen}^{(i)} = 0 \qquad (4\text{-}1)$$

where i represents the name of component. F stands for the mass flow rate in the metric tons per year. The overall mass balance is the summation of all components mass balances.

The steady state overall energy balance is established based on the first law of thermodynamics. Neglecting changes in kinetic and potential energy, this equation is (Felder and Rousseau, 1986):

$$\Delta H = Q - W \qquad (4\text{-}2)$$

where Q is the net heat added to the system; W is the work done by the system on the surroundings; and ΔH is the change in enthalpy between input and output streams, i.e.,

$$\Delta H = \sum_{output} n^{(i)} H^{(i)} - \sum_{input} n^{(i)} H^{(i)} \qquad (4\text{-}3)$$

The reference condition for enthalpy is the elements that constitute the reactants and products at 25°C and the nonreactive molecular species at any convenient temperature. $H^{(i)}$ for a reactant or product is the sum of the heat of formation of the species at 25 °C and any sensible and latent heats required to bring the species from 25 °C to its inlet or outlet state. The reaction term is not required if elements are chosen as references, since this term is implicitly calculated when the heats of formation of the reactants are subtracted from those of the products.

Q is the net heat transferred to the process. It includes heat input in the form of steam in the heat exchanger and distillation column reboilers, and heat output which is removed by cooling water in heat exchanger and distillation column condensers. The heat output by cooling water can be estimated from HYSYS simulation and other sources as Q_{out} (energy per mass of reactant) times F_r (mass flow rate of reactant). Then the heat input by steam is Q_{in}, and the equation for Q can be written as Equation 4-4.

$$Q = Q_{in} - Q_{out} \times F_r \qquad \text{(r is for reactant)} \qquad (4\text{-}4)$$

where Q_{out} is a positive number. The negative sign indicates heat is removed from the process. The energy balance becomes Equation 4-5.

$$\sum_{output} n^{(i)}H^{(i)} - \sum_{input} n^{(i)}H^{(i)} = Q_{in} - Q_{out} \times F_r \qquad (4\text{-}5)$$

This form of the energy balance is used in the process models. Q_{in} is calculated from the solution obtained by the System, and it represents the heat required for separations and steam required for chemical reaction for an endothermic reaction in the chemical reactor. For an exothermic reaction, Q_{in} is the net of the heat released by the reaction and steam required for separations. Steam and heat required for chemical reactions are at a temperature level significantly above the temperature of heat removed by cooling water (~ 40^oC). Also, shaft work for electricity energy for pumps and compressors is typically small compared to the other energy flows and is not included.

The expression for enthalpy is always expressed as a function of temperature (Equation 4-6).

$$H_k^i(T) = (a_1^i + \frac{1}{2}a_2^i T + \frac{1}{3}a_3^i T^2 + \frac{1}{4}a_4^i T^3 + \frac{1}{5}a_5^i T^4 + \frac{b_1^i}{T})RT \quad \text{J/mol} \qquad (4\text{-}6)$$

where a_1, a_2, a_3, a_4 ,a_5, and b_1 are coefficients; R is gas constant; T is temperature; i stands for species; and k stands for streams. The detailed enthalpy function for the species in the chemical production complex are given in Appendix A.

The next section describes the existing plants in the chemical production complex in the lower Mississippi River corridor as shown in Figure 3.3 called base case. A list of all of the stream designation and definition is given in Table B-1 of Appendix B, and stream splits and mixing parts are given in Table 4-46.

B. Processes in the Existing Chemical Production Complex - Base Case

The chemical companies with the existing chemical plants are given in Table 4-1. In this table, the capacities in the left column are given by the industrial advisors (Hertwig, 2004), and these values were used in the simulation of the complex. The capacities given in the right column in Table 4-1 were from Louisiana Chemical & Petroleum Products List (1998) for the plants in the lower Mississippi River corridor.

B-1. Sulfuric Acid (Hertwig, 2004; Louisiana Chemical & Petroleum Products List, 1998)

In the chemical production complex, there is one option for sulfuric acid production, which is the contact process for sulfuric acid. The contact process is described below in detail. In the chemical production complex in the lower Mississippi River corridor the sulfuric acid production plants are as follow (Louisiana Chemical & Petroleum Products List, 1998).

- IMC-Agrico, Uncle Sam (2.2 million metric tons per year)
- IMC-Agrico, Faustina (1.1 million metric tons per year);
- PCS Nitrogen Fertilizer LP, Geismar (454 thousand metric tons per year);
- Dupont, Burnside (420 thousand metric tons per year);
- Rhodia, Baton Rouge (725 thousand metric tons per year);
- Cytec Industries, Westwego (572 thousand metric tons per year);

For the chemical production, the capacity of 10,932 tons per day was used in the base case (Hertwig, 2004).

Table 4-1 Chemical Companies and Plant Capacities in the Chemical Production Complex, from Hertwig (2004) and Louisiana Chemical & Petroleum Products List (1998)

Processes and Capacities (Hertwig, 2004)	Companies and Plants (Louisiana Chemical & Petroleum Products List, 1998)
Phosphoric acid (3833 tons per day)	• IMC-Agrico, Uncle Sam (805 thousand metric tons per year) • IMC-Agrico, Faustina (525 thousand metric tons per year) • PCS Nitrogen Fertilizer LP, Geismar (200 thousand metric tons per year) • Rhodia, Geismar (90 thousand metric tons per year)
Sulfuric acid (10,932 tons per day)	• IMC-Agrico, Uncle Sam (2.2 million metric tons per year) • IMC-Agrico, Faustina (1.1 million metric tons per year) • PCS Nitrogen Fertilizer LP, Geismar (454 thousand metric tons per year) • Dupont, Burnside (420 thousand metric tons per year) • Rhodia, Baton Rouge (725 thousand metric tons per year) • Cytec Industries, Westwego (572 thousand metric tons per year)

Table 4-1 Continued

Processes and Capacities (Hertwig, 2004)	Companies and Plants (Louisiana Chemical & Petroleum Products List, 1998)
Ammonia (1,986 tons per day)	• IMC-Agrico, Faustina Plant (480 thousand metric tons per year) • CF Industries, Donaldsonville (1.84 million metric tons per year) • Triad Nitrogen, Donaldsonville (1.02 million metric tons per year) • BCP, Geismar (400 thousand metric tons per year) • PCS Nitrogen Fertilizer LP, Geismar (550 thousand metric tons per year) • Monsanto, Luling (440 thousand metric tons per year) • Cytec, Westwego (385 thousand metric tons per year) • Air Product & Chemicals Inc., St. Gabriel (270 thousand metric tons per year)
Nitric acid (from NH_3) (539 tons per day)	• CF industries, Donaldsonville (380 thousand tons per year) • PCS Nitrogen Fertilizer LP, Geismar (923 thousand tons per year) • Rubicon, Geismar (120 thousand tons per year)
Ammonium nitrate (684 tons per day)	• PCS Nitrogen, Geismar (485 thousand metric tons per year) • CF Industries, Donaldsonville (340 thousand metric tons)
Urea (301 tons per day)	• IMC-Agrico, Faustina Plant (260 thousand tons per year) • CF Industries, Donaldsonville (1.6 million tons per year) • BCP, Geismar (220 thousand tons per year) • PCS Nitrogen Fertilizer LP, Geismar (412 thousand tons per year) • Cytec Industries, Westwego (120 thousand tons per year) • Triad Nitrogen, Donaldsonville (420 thousand tons per year)
Urea ammonium nitrate solutions (183 tons per day)	• CF Industries, Donaldsonville (770 thousand metric tons per year) • PCS Nitrogen Fertilizer LP, Geismar (1.1 million metric tons per year)
Methanol (548 tons per day)	• BCP, Geismar (330 million gallons per year) • Ashland, Plaquemine (160 million gallons per year) • Cytec, Westwego (Not available) • Georgia Gulf, Plaquemine (160 million gallons per year) • Praxair, Geisamr (10 million gallons per year)

Table 4-1 Continued

Processes and Capacities (Hertwig, 2004)	Companies and Plants (Louisiana Chemical & Petroleum Products List, 1998)
MAP (885 tons per day)	• IMC-Agrico, Faustina (Not available)
DAP (5,666 tons per day)	• IMC-Agrico, Taft (600 thousand tons per year for DAP) • Avondale Ammonia, Westwego (125 thousand metric tons per year for DAP)
GTSP (2,259 tons per day)	• IMC-Agrico, Faustina (Not available)

B-1-1. Process Description of Contact Process for Sulfuric Acid

B-1-1-1. Sulfur Feedstock

There are two ways to obtain sulfur feedstock, Frasch and Claus processes.

Frasch process: In this process 160°C water is injected via double-pipe annulus into a porous sulfur-bearing rock formation and melted sulfur returns (along with some hot water) in the center pipe. Sulfur-melting water is heated in natural-gas-fired package boilers. This water is fresh onshore and sea/salt offshore. This sulfur well is typically called a "mine". However, Frasch sulfur is no longer practiced with excess Claus sulfur available. It is still in the model for the completeness.

Claus sulfur: There are two reactions in this process.

$$H_2S\ (g) + 1.5O_2 = SO_2\ (g) + H_2O\ (g) \tag{4-7}$$

$$SO_2\ (g) + 2H_2S\ (g) = 3S(l) + 2H_2O\ (g) \tag{4-8}$$

H_2S is recovered from sour natural gas and oil refining by absorbing it, then releasing it in fairly pure form. Environmental permits require 98% conversion of H_2S in 1984

(99.5% in Alberta province). Also environmental permits presume the balance is SO_2 air emissions.

B-1-1-2. Sulfur Storage

Trace hydrocarbon content in sulfur will react with S to produce H_2S, which must be air-stripped to prevent accumulation of lethal or explosive levels of H_2S.

B-1-1-3. Sulfuric Acid Reaction Theory

The contact process is a three-step process that produces sulfuric acid and steam from air, molten sulfur and water, i.e. the feed preparation, the reaction and the absorption. The block diagram is shown in Figure 4.2 with the steam definitions in Table 4-2.

The feed preparation equipment includes an air filter, air-drying tower, a main compressor and a sulfur burner. Molten sulfur feed is combusted with dry air in the sulfur burner which goes to completion. The reaction is:

$$\mathrm{S} + \mathrm{O}_2 = \mathrm{SO}_2 + \mathrm{Heat} \tag{4-9}$$

The burner-exit gas is composed of sulfur dioxide, nitrogen, carbon dioxide, Ar, and unreacted oxygen at 1,800-2,100 ^{o}F. Much of the heat of reaction is recovered in a waste heat boiler. The compressor is power by a steam-driven turbine that has an efficiency of about 65% for the turbine itself.

For the reaction part there is a four (or five) - bed reactor packed with two different types of vanadium pentoxide catalyst where the gas mixture from the feed preparation section is further oxidized to produce sulfur trioxide according to the reaction:

$$2SO_2 + O_2 = 2SO_3 + \text{Heat} \tag{4-10}$$

This is where the "contact" comes from. The alternate process is "chamber" and that has not been run for decades, and all further references to "contact" are dropped.

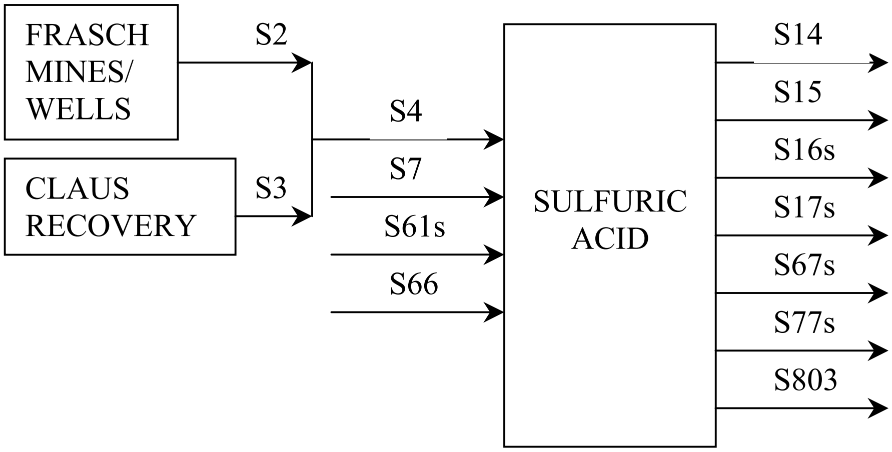


Figure 4.2 Block Diagram of Contact Process to Produce Sulfuric Acid

Table 4-2 Description of Process Streams in Contact Sulfuric Acid Production

Name of Streams	Description
Input Streams	
S2	S from Frasch mines/wells to sulfuric acid process (SAP)
S3	S from Claus recovery to SAP
S4	Total S to SAP
S7	Dry air to SAP
$S61_S$	Boiler feed water (BFW) to SAP
S66	Process water to SAP
Output Streams	
S14	H_2SO_4 solution produced from SAP
S15	Vent gases exiting from SAP
$S16_S$	Low pressure steam (LP) (40 psig) exiting from SAP
$S17_S$	High pressure steam (HP) (600 psig) exiting from SAP
$S67_S$	Boiler blowdown H_2O from SAP
$S77_S$	Intermediate pressure steam (IP) (150 psig) exiting from SAP
S803	Impurity of sulfur from SAP

Reaction 4-10 is exothermic, and the equilibrium conversion decreases with the increase in reaction temperature. The process uses multiple packed beds with heat exchangers between each bed to remove the liberated heat to reduce the temperature to allow further conversion. With the equilibrium constant $K_p = \frac{P_{SO_3}}{P_{SO_2} P_{O_2}^{0.5}}$, conversion is raised by adding interstage SO_3 absorption. With interstage absorption, P_{SO_3} is lower downstream and P_{SO_2} can be raised upstream by increasing burner-feed sulfur-to-air ratio.

In the absorbers, intermediate and final, essentially all of the SO_3 present is absorbed from the reaction gas mixture into 98.5wt% sulfuric acid to produce more concentrated acid and heat of absorption according to the equation:

$$SO_3 + H_2O = H_2SO_4 + \text{Heat} \tag{4-11}$$

The equipment in this part includes the final acid absorption tower, inter-pass absorption tower, acid pump tank(s), dilution acid tank (optional) and heat exchangers which are one acid cooler per tower, gas-to-gas heat exchanger(s), and/or economizers or superheaters on gas streams to each absorber.

B-1-1-4. Air-Drying and SO_3-Adsorption Towers

Commercial processes add SO_3 to 98.5% H_2SO_4 and water to obtain 99% H_2SO_4. SO_3 absorption is maximized and essentially complete using 98.5% H_2SO_4.

Poorer-than-normal absorption can make the stack gas visible as a white plume of H_2SO_4 mist. Stack gas opacity is a concern because there are limits in the operating permit, and opacity may indicate a steam-system leak. High-performance demisters will capture some of the mist and hide the steam-system problems for a while. Other potential causes for opacity include low absorber acid temperature and high absorber gas-inlet temperature.

Product H_2SO_4 can be produced as dilute as 93% with little extra risk of corrosion. Corrosion accelerates rapidly below 92%. Lower strengths (93% vs 98.5%) are valuable only to reduce heat of dilution in subsequent use.

Air drying is needed to reduce risk of acid condensing in the gas-side of the process. Air is dried with H_2SO_4. To improve drying, cooler acid is much better and 98.5% is slightly better than 93%. Dew point is typically about -40°C and can be estimated from H_2SO_4 partial-pressures tables.

B-1-1-5. Waste Heat Recovery

Waste heat is recovered from gas streams above 300°F as 600 or 900 psig superheated steam. Heat recovery from gas upstream of acid is limited by the gas dew point of 280-300°F. Dew point depends on the hydrocarbon content of the sulfur feed and drops about 20°F after being dried in the first SO_3-absorption tower. The 300 psig gap in steam-system designs (600 or 900 psig) is because turbine metallurgy must be more exotic above 750°F which is a reasonable superheat for 600 psig steam. Increasingly, lower-grade heat is recovered at an intermediate pressure. Heat of SO_3 absorption can be recovered with Monsanto Enviro-Chem's heat recovery system (HRS). This heat is recovered as steam at up to 150 psig. Process heat recovery is about 70% without HRS and about 80% with HRS. Most losses go to acid-cooling water.

B-1-1-6. Production Rates

H_2SO_4-STPD (short tons per day) -to-steam-KPPH (thousand pounds per hour) production ratio runs 9.2±0.5 without HRS. The ratio changes with ambient temperature, wind, rain, and fuel-to-air ratio, which is adjusted to keep stack SO_2 within environmental permit limits. H_2SO_4 production capacity is normally limited by blower capacity and increases at night and in winter when inlet air is denser because it is cooler.

B-1-2. Material Balance and Energy Balance

The material balance and energy balance equations for this process are given in Table 4-4. There are some parameters (Table 4-3) referred to Figure 4.2 for its material balance. In the constraints of Table 4-4, F denotes the component mass flow rate, metric tons per year (MTPY), and its superscript i and subscript k denote the component names and stream numbers, respectively.

Table 4-3 Parameters in Sulfuric Acid Production, from Hertwig (2004)

Name	Meaning	Value
SIPSA	S impurity (decimal fraction)	0.001
SO2EMSA	Stack SO_2 emissions, lb SO_2 / short ton H_2SO_4 produced (max 4.0 per short ton)	4.0
BBLSA	Boiler blowdown as fraction of boiler feed water (BFW) (typical = 0.05-0.10)	0.08
SHPSA	Short TPD H_2SO_4/ (Klb/hr of HP drum steam)	9.1
HPBTSA	Fraction of high pressure (HP) drum steam used by blower turbine (typically = 0.35-0.60)	0.40
IPCAPSA	Fraction of SAP capacity with heat recovery system producing intermediate pressure (IP) steam	0.3
CONCSASA	Sulfuric product concentration (0.93 (produced in drying tower or in dilution tank) - 0.99; 0.985 (for final abstraction tower) minimizes stack opacity)	0.985
IPHRSSA	Klb/hr IP steam (from a 3085 TPD SAP with heat recovery system (HRS))	150

Table 4-4 Constraint Equations for Contact Sulfuric Acid Production

Material Balances	
Overall	$(F_4 + F_7 + F_{S61} + F_{66}) - (F_{14} + F_{15} + F_{S16} + F_{S17} + F_{S67} + F_{S77} + F_{803}) = 0$
	where $F_7 = F_7^{(O_2)} + F_7^{(N_2)} + F_7^{(CO_2)} + F_7^{(Ar)}$
	$F_{14} = F_{14}^{(H_2SO_4)} + F_{14}^{(H_2O)}$
	$F_{15} = F_{15}^{(N_2)} + F_{15}^{(Ar)} + F_{15}^{(CO_2)} + F_{15}^{(SO_2)}$
Heat Exchange (boiler feed water and steam balance)	
	$(F_{S16} + F_{S17} + F_{S67} + F_{S77}) - F_{S61} = 0$
	$F_{S61} = F_{S61}^{(a)} + F_{S61}^{(b)}$
Species	S : $F_4(1 - SIPSA) - \frac{32.06}{98.08} F_{14}^{(H_2SO_4)} - \frac{32.06}{64.06} F_{15}^{(SO_2)} = 0$
	H_2O(process water) : $F_{66} - \frac{18.02}{98.08} F_{14}^{(H_2SO_4)} - F_{14}^{(H_2O)} = 0$
	O_2 : $F_7^{(O_2)} - (1.5)\frac{32}{98.08} F_{14}^{(H_2SO_4)} - \frac{32}{64.06} F_{15}^{(SO_2)} = 0$
	N_2 : $F_{15}^{(N_2)} - F_7^{(N_2)} = 0$
	Ar : $F_{15}^{(Ar)} - F_7^{(Ar)} = 0$
	CO_2 : $F_{15}^{(CO_2)} - F_7^{(CO_2)} = 0$
	SO_2 : $\frac{SO2EMSA}{2000} F_{14}^{(H_2SO_4)} - F_{15}^{(SO_2)} = 0$
	Impurity: $F_{803} = F_4 \times SIPSA$
Heat Exchange	BFW: $F_{S61}^{(a)} - \frac{(F_{S16} + F_{S17})}{(1 - BBLSA)} = 0$
	HP: $F_{S17} - \frac{(12)(1 - HPBTSA)}{SHPSA} F_{14}^{(H_2SO_4)} = 0$
	IP: $F_{S77} - \frac{IPCAPSA \times IPHRSSA(12)}{(3400)} F_{14}^{(H_2SO_4)} = 0$
	LP: $F_{S16} - \frac{(12)HPBTSA}{SHPSA} F_{14}^{(H_2SO_4)} = 0$
	Blowdown H_2O: $F_{S67} = BBLSA \times F_{S61}^{(a)}$

Table 4-4 Continued

Energy Balance	
Overall	$(\frac{1}{M^{(H_2O)}}F_{S61}^{(H_2O)}H_{S61}^{(H_2O)} - (F_{S16}H^{(LP)} + F_{S17}H^{(HP)} + F_{S77}H^{(IP)}$ $+\frac{1}{M^{(H_2O)}}F_{S67}^{(H_2O)}H_{S67}^{(H_2O)})) - Q_{SACID} = 0$ where M^i is molecule weight, i= H_2O
Enthalpy Function	$H_k^i(T) = (a_1^i + \frac{1}{2}a_2^iT + \frac{1}{3}a_3^iT^2 + \frac{1}{4}a_4^iT^3 + \frac{1}{5}a_5^iT^4 + \frac{b_1^i}{T})RT$ J/mol where R is gas constant T is temperature $i = H_2O$ $k = 61, 67$ $H^{(LP)}(T) = ((72.558 + (0.5)(-0.66244)T + (\frac{1}{3})(0.002562)T^2 +$ $(0.25)(-4.3659E-06)T^3 + (0.2)(2.7818E-09)T^4 + \frac{(-41886)}{T})(8.3145)T$ $-1893)\frac{1}{18.02} + ((-0.007)T^2 + (2.7838)T + 2292.0563)$ J/g $H^{(IP)}(T) = ((72.558 + (0.5)(-0.66244)T + (\frac{1}{3})(0.002562)T^2 +$ $(0.25)(-4.3659E-06)T^3 + (0.2)(2.7818E-09)T^4 + \frac{(-41886)}{T})(8.3145)T$ $-1893)\frac{1}{18.02} + ((-0.007)T^2 + (2.7838)T + 2292.0563)$ J/g $H^{(HP)}(P,T) = 2.326((5.32661)((T-273.15)(1.8)+32) - 0.2839015P$ $-(7.352389E-03)((T-273.15)(1.8)+32)^2 + (3.581547E-06)$ $((T-273.15)(1.8)+32)^3 - (7.289244E-05)P^2 + (4.595405E-04)$ $((T-273.15)(1.8)+32)P) - 15861.82$ J/g, P:psia Note: LP and IP have no superheat, from Meyer, et al. (1977) and McBride, et al. (1993); HP has superheat, from Chen (1998).

In Table 4-4, the overall material balance for the whole process is given with the boiler feed water and steam balance in heat exchange part of the process. For the species material balance obtained using the reaction equations (4-9, 4-10 and 4-11), the first equation is for the sulfur balance; the second one is for the process water balance; the third one is for the oxygen balance; the fourth one is for the nitrogen balance; the fifth one is for the argon balance; the sixth one is for carbon dioxide balance; the last one is for the impurity balance, i.e., the impurity in the sulfur input is treated as an inert.

In the heat exchange part, all the streams starting with subscript S in Table 4-4 plus some number are steam and boiler feed water flow rates. They are only for heat exchange and are not reactants. Those equations in the heat exchanger are for the mass balance of steam and water. All of these steam outputs will be used as heat output by steam in the energy balance part. The first equation is for the boiler feed water (BFW) balance; the second one is for the high pressure steam (HP) balance; the third one is for the intermediate pressure steam (IP) balance; the fourth one is for the low pressure steam (LP) balance which equals the fraction of HP going to blower turbine; and the last one is for blowdown water balance to control scaling.

In the overall energy balance in Table 4-4, Q_{SACID} is the net of the heat released by the reactions (Equation 4-9 and 4-10). This energy is recovered in the waste boiler and is used by other processes in the chemical production complex. Q_{SACID} is calculated from the net steam output from the plant and does not include cooling water in the acid cooler. It is different from the energy balance method using the enthalpy changes from input reactants to output reactants and heat loss (Equation 4-2, 4-3, 4-4, and 4-5) because sulfuric acid plant can produce the steam output in the form of HP, IP and LP as given by the Heat Exchange equations in Table 4-4. HP and IP are used in the power plant to generate electricity and LP. LP is used to evaporate the phosphoric acid from 28% to 48% in the phosphoric acid plant. In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 23 variables and 23 equations, including one dependent one (overall material balance). So the number of degrees of freedom is 1 for the material balance part. For the material and energy balances, there are 35 variables and 29 equations, including one dependent one (overall material balance). The number of degrees of freedom is 7.

B-2. Phosphoric Acid (H_3PO_4) Production (Wet Process) (Austin, 1984; Hertwig, 2004; Louisiana Chemical & Petroleum Products List, 1998)

The raw material for phosphoric acid production is phosphate rock ($CaF_2 \cdot 3Ca_3(PO_4)_2$, a fluorapatite). Although not included in the chemical production complex, phosphate rock is strip mining using giant draglines to remove overburden whose phosphatic value is too low for economic processing, placing it to the side, usually in a mined-out area. Then the dragline digs the phosphate rock matrix and dumps it in a pit where the rock is slurried by giant water jets for pumping to a beneficiation plant miles away. The matrix is composed of clay slimes, silica sand and phosphate pebble. Phosphate rock purity is measured as BPL or bone phosphate of lime as percent of pure $Ca_3(PO_4)_2$(Austin, 1984). Phosphate concentration in rock, acid, or fertilizers is usually referred to on its anhydrous basis, percent of P_2O_5. For example, 100% H_3PO_4 would be $(\frac{142}{2\times 98}\times 100\% =) 72.4\%$ P_2O_5. Sand removed goes to reclaim old strip mines. Clay slimes removed go to large settling ponds. Clay fractions carry significant amount of phosphate for which there is not an economical recovery process today.

In the existing chemical production complex, phosphoric acid is produced by the wet process. In the chemical production complex of the lower Mississippi River corridor, the companies producing phosphoric acid by wet process are as follow (Louisiana Chemical & Petroleum Products List, 1998).

- IMC-Agrico, Uncle Sam (805 thousand metric tons per year)
- IMC-Agrico, Faustina (525 thousand metric tons per year)
- PCS Nitrogen Fertilizer LP, Geismar (200 thousand metric tons per year)
- Rhodia, Geismar (90 thousand metric tons per year)

For the chemical production, the capacity of 3,833 tons per day was used in the base case (Hertwig, 2004).

Two other options are included in the superstructure, electric furnace process and Haifa process, which will be described in the complex extension part. The description of the wet process is given below.

B-2-1. Process Description

B-2-1-1. Reaction Theory - Digestion, Filtration, Evaporation and Clarification

In the wet process, phosphate rock is digested in H_2SO_4 to swap H^+ and Ca^{2+}. Digestion is conducted in a stirred chemical reactor with multi-compartments (called "attack" tank). Soluble H^+ is moved from the SO_4^{2-} to the PO_4^{3-}. Insoluble Ca is moved from the PO_4^{3-} to the SO_4^{2-}. Digestion is controlled to promote large and filterable gypsum crystals since filtration is the rate-limiting step. Product acid contains residual $CaSO_4 \cdot 2H_2O$ as solids (gypsum) as well as in solution. Careful control of digestion and clarification can maximize removal of $CaSO_4 \cdot 2H_2O$. Rock contains many impurities, especially F, Fe, Al, Mg and Si. Most of the Fe, Al, and Mg remain in solution, moving with the phosphoric acid into the downstream phosphates. Digestion product strength is typically 25-29% P_2O_5. Digestion product is usually evaporated to 45-55% P_2O_5 to help the water balance during ammoniation to produce solid/granular products and to allow for additional purge of impurities $CaSO_4 \cdot 2H_2O$ and F. SiF_4 is scrubbed from digestion fumes and evaporator vapors. Evaporator scrubbings are often recovered for salable H_2SiF_6.

Management of byproduct gypsum is a major environmental concern, mostly for gypsum's P, F and Radon contents. Gypsum is typically stacked 50-300 feet high on hundreds of acres next to the phosphoric acid plant. To minimize groundwater contamination, any sandy ground must be covered with clay or plastic before starting a new stack. Also, after the stack is as high as practical, it is covered with soil and grass to minimize contamination of runoff water.

The wet process block diagram is shown in Figure 4.3 with the definitions of streams shown in Table 4-5. The key reactions are:

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O = 3CaSO_4 \cdot 2H_2O + 2H_3PO_4 \quad (4\text{-}12)$$

$$CaF_2 + H_2SO_4 + 2H_2O = CaSO_4 \cdot 2H_2O + 2HF \quad (4\text{-}13)$$

The general reaction from the summation of 3 times reaction equation (4-12) plus one times (4-13) is

$$CaF_2{\cdot}3Ca_3(PO_4)_2 + 10H_2SO_4 + 20H_2O = 10CaSO_4{\cdot}2H_2O + 6H_3PO_4 + 2HF \quad (4\text{-}14)$$

where $CaF_2{\cdot}3Ca_3(PO_4)_2$, is the fluorapatite.

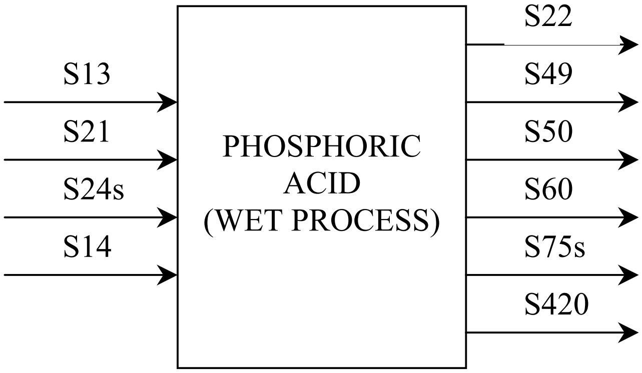


Figure 4.3 Block Diagram of Wet Process to Produce Phosphoric Acid

Table 4-5 Description of Process Streams in Wet Process

Name of Streams	Description
Input Streams	
S13	Phosphate rock slurry to phosphoric acid plant (PAP)
S21	Gypsum stack decant water to PAP
$S24_S$	LP steam to PAP
S14	Sulfuric acid to PAP
Output Streams	
S22	Slurried gypsum produced from PAP
S49	H_2SiF_6 solution produced from fluorides scrubbers in PAP
S50	Other inert materials in the phosphate rock from PAP
S60	Total phosphoric acid produced in PAP
$S75_S$	Condensate water from LP input in PAP
S420	Water evaporated from digestion and filtration in PAP

B-2-1-2. Fluoride Scrubbers

F is scrubbed because discharge to offsite water streams is regulated and because there is a market for the product. Fluorine fumes are drawn from the attack tank and filter, and scrubbed and recovered with H_2SiF_6 solution to which water is added. What is not scrubbed will go with the evaporator's barometric condenser water. This water is typically once-through river water or closed-circuit gypsum-pond water. The following reactions take place:

$$6HF + SiO_2 = H_2SiF_6 + 2H_2O \tag{4-15}$$

Reaction (4-15) is with small amount of fine sand present in feed rock. Most domestic phosphate rock has an excess of SiO_2 vs F. Heating under vacuum in an evaporator (or addition of strong acid like H_2SO_4) will shift reaction (4-16) to the right.

$$H_2SiF_6 = SiF_4 + 2HF \tag{4-16}$$

Scrubbing reaction (4-17) produces 1 mole of SiO_2 that will precipitate unless there are 6 more moles of HF present to react with it to form 1 more mole of H_2SiF_6 via reaction (4-15).

$$3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2 \tag{4-17}$$

B-2-2. Material Balance and Energy Balance

Table 4-6 shows the parameters used in the material balance and energy balance (Table 4-7). Rock slurry is typically 66-68wt % solids. The percent is high enough to minimize water entering the process here in order to maximize water fed at filter wash where P_2O_5 gets recovered. The percent is low enough to let the cyclones or screens in the mill circuit give a good separation. The oversize is recycled back to the mill. Today's typical sulfuric acid concentration is 98%. Higher-than-98.5% will give poorer SO_3 absorption in the sulfuric plant (risks SO_3 emissions and visible stack plume) and lower than 93% accelerates corrosion of carbon steel. Typical P_2O_5 loss is

3-6%. Losses include undigested rock, P_2O_5 trapped in gypsum crystals, and aqueous P_2O_5 incompletely washed from the gypsum filter cake. Per ton of 64 BPL rock, 0.62 ton of [100%] H_2SO_4 is consumed to digest phosphate. The $CaCO_3$ present (a variable amount not tied to BPL) raises the actual ratio to about 0.802 T H_2SO_4 per T rock, which is roughly the 0.80 T H_2SO_4 / T rock used below.

Table 4-6 Parameters in Wet Process for Phosphoric Acid Production, from Hertwig (2004)

Name	Meaning	Value
DFPAP	P_2O_5 digested fraction	0.98
NRPPAP	Net P_2O_5 recovery in digestion and filtration	0.96
RBPLPAP	Fraction of pure $Ca_3(PO_4)_2$ (BPL/100)	0.64
FPBPPAP	Fraction of 28% H_3PO_4 bypassing the evaporators	0.00
EFCPAP	Evaporator feed strength %P_2O_5 (26-29%)	28%
EPCAP	Evaporator product strength %P_2O_5 (45-54%)	48%
ESEPAP	Evaporator steam efficiency lb water evaporated per lb steam condensed	0.80
FASPAP	Fluosilicic acid concentration(weight fraction)	0.24
FFEPAP	Fraction of F evaporated in evaporators (0.3-0.8)	0.60
FEFPAP	Fraction of evaporators with F scrubbers	0.80
C_1	T rock per T P_2O_5 produced	3.56
C_2	H_2SO_4 to rock ratio (T 100% H_2SO_4 / T 64-BPL rock)	0.80
C_3	T gypsum produced per T P_2O_5 produced	4.18
C_4	Net fraction of all fluorine recovered	0.36

In Table 4-7, the overall material balance for the whole process is given with the expressions of the process streams. For the species material balance obtained using the reaction equations (4-12, 4-13, 4-14, 4-15, 4-16 and 4-17), the first equation is for the P_2O_5 balance; the second one is for the sulfuric acid balance; the third one is for the gypsum balance; the fourth one is for the overall process water balance (H_2O-1); the fifth one is for the process water evaporation balance (H_2O-2); the last one is for the fluoride balance for the whole process. In the heat exchange part, the first equation

Table 4-7 Constraint Equations for the Phosphoric Acid Wet Process

Material Balance	
Overall	$(F_{13}+F_{14}+F_{21}+F_{S24})-(F_{22}+F_{60}+F_{S75}+F_{49}+F_{50}+F_{420})=0$
	where $F_{14}=F_{14}^{(H_2SO_4)}+F_{14}^{(H_2O)}$
	$F_{60}=F_{60}^{(H_2O)}+F_{60}^{(P_2O_5)}$
	$F_{49}=F_{49}^{(H_2SiF_6)}+F_{49}^{(H_2O)}$
Species	P_2O_5 : $\frac{1}{C_1}F_{13}-F_{60}^{(P_2O_5)}=0$
	H_2SO_4 : $F_{14}^{(H_2SO_4)}-F_{13}C_2=0$
	Gypsum: $F_{60}^{(P_2O_5)}C_3-F_{22}=0$
	H_2O-1: $F_{14}^{(H_2O)}+F_{21}-((F_{60}^{(H_2O)}-\frac{(3)(18.02)}{141.94}F_{60}^{(P_2O_5)})+F_{420}+F_{49}^{(H_2O)})$ $+\frac{(2)(18.02)}{144.11}F_{49}^{(H_2SiO_6)}=0$
	H_2O-2: $F_{60}^{(P_2O_5)}(\frac{1}{EFCPAP}-\frac{1}{EPCPAP})-F_{420}=0$
	F: $\frac{(RBPLPAP)(2)(144.11)C4}{(310.18)(3)(6)}F_{13}-F_{49}^{(H_2SiF_6)}=0$
Heat Exchange	LP-1 : $F_{S24}-\frac{F_{420}}{ESEPAP}=0$
	LP-2 : $F_{S75}-F_{S24}=0$
Energy Balance	
Overall	$(F_{S24}H^{(LP)}-\frac{1}{M^{(H_2O)}}F_{S75}^{(H_2O)}H_{S75}^{(H_2O)})-Q_{PPA}=0$
	where $M^{(i)}$ is molecule weight. $i = H_2O$
Enthalpy Function	$H_k^i(T)=(a_1^i+\frac{1}{2}a_2^iT+\frac{1}{3}a_3^iT^2+\frac{1}{4}a_4^iT^3+\frac{1}{5}a_5^iT^4+\frac{b_1^i}{T})RT$ J/mol
	$i=H_2O$; $k=75$
	$H^{(LP)}(T)=((72.558+(0.5)(-0.66244)T+(\frac{1}{3})(0.002562)T^2+(0.25)(-4.3659E-06)T^3+(0.2)(2.7818E-09)T^4+\frac{(-41886)}{T})(8.3145)T-1893)\frac{1}{18.02}+((-0.007)T^2+(2.7838)T+2292.0563)$
	J/g, LP has no superheat, from Meyer, et al. (1977) and McBride, et al. (1993)

is the steam requirement for the process (LP-1) and the other is steam input and output balance (LP-2). The steam input ($S24_S$) was from $S16_S$ (sulfuric acid plant) and $S18_S$ (power plant). The steams in the heat exchanger were used in the energy balance part.

In the overall energy balance, Q_{PPA} is equal to the heat from LP steam to evaporate the phosphoric acid from 28% to 48% in the phosphoric acid plant. Also, this steam is the only heat input for the process. Hence, Q_{PPA} is calculated directly from this LP steam input required to concentrate the phosphoric acid. The $Q_{out} \times F_r$ term in Equation 4-5 is not required since no cooling water is used in this process.

In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 16 variables and 15 equations, so the number of degrees of freedom is 1 for the material balance part. For the material and energy balance, there are 21 variables and 18 equations, so the number of degrees of freedom is 3.

B-3. Granular Triple Super Phosphate (GTSP) (Hertwig, 2004; Austin, 1984; Brown, et al., 1985)

B-3-1. Process Description

In the chemical production complex in the lower Mississippi River corridor, granular triple super phosphate is produced by IMC-Agrico with the capacity of 2,259 tons per day (Hertwig, 2004). GTSP is made by the action of phosphoric acid on phosphate rock. This can be expressed as:

$$Ca_3(PO_4)_2 + 4H_3PO_4 = 3Ca(H_2PO_4)_2 \quad \text{digestion (not including F in rock)} \qquad (4\text{-}18)$$

$$CaF_2 + 2H_3PO_4 = Ca(H_2PO_4)_2 + 2HF \quad \text{(the F content)} \qquad (4\text{-}19)$$

The general reaction from the summation of 3 times reaction equation (4-18) and 1 times reaction equation (4-19) is Equation (4-20), where $CaF_2 \cdot 3Ca_3(PO_4)_2$ is the mineral fluorapatite.

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 14H_3PO_4 = 10Ca(H_2PO_4)_2 + 2HF \quad \text{digestion} \qquad (4\text{-}20)$$

The block diagram is given in Figure 4.4 with the stream descriptions from Table 4-8. Pulverized phosphate rock is mixed with phosphoric acid in a two-stage reactor. The resultant slurry is sprayed into the granulator. The granulator contains recycled fines from the process. The product from the granulator is dried in the dryer with heat input, screened, crushed if oversize, and cooled again in the cooler by cooling water. The final product is conveyed to bulk storage where the material is cured for 4 to 6 weeks during which time a further reaction of acid and rock occurs which increases the availability of P_2O_5 as plant food. The exhaust gases from the granulator and cooler are scrubbed with water to remove silicofluorides which are represented in this material balance as HF (Austin, 1984).

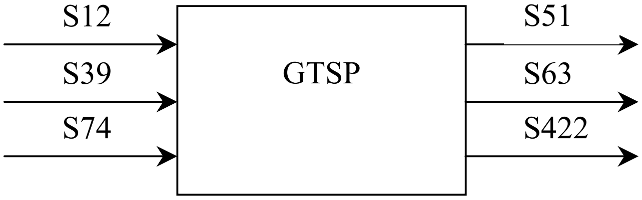


Figure 4.4 Block Diagram of GTSP Plant

B-3-2. Material Balance and Energy Balance

Using the parameters in Table 4-9, the material balance and energy balance of GTSP plant are given in Table 4-10.

In Table 4-10, first the overall material balance for this process is given. For the species material balance obtained using the reaction equations (4-18, 4-19 and 4-20), the first equation is for the P_2O_5 balance; the second one is for the rock balance; the third one is for the HF balance; the last one is for the water balance.

Table 4-8 Description of Process Streams in GTSP Plant

Name of Stream	Description
Input Streams	
S12	Phosphate rock to GTSP
S39	Wet process phosphorous acid to GTSP
S74	Inert impurity to GTSP
Output Streams	
S51	GTSP produced from GTSP
S63	HF produced from GTSP
S422	Water evaporated from GTSP

Table 4-9 Parameters in GTSP Production, from Hertwig (2004)

Name	Meaning	Value
UPAGTSP	Utilization of H_3PO_4 in GTSP plant	0.999
PGTSP	GTSP fraction of P_2O_5 (0.45-0.46) (weight fraction)	0.46
BPLGTSP	Rock BPL(%)	75
URGTSP	Rock utilization	0.999

In the overall energy balance, Q_{GTSP} is the heat input for the process, such as the heat required to dry the product in the dryer, which is calculated from the energy balance. Q_{out} is the heat loss of unit operations in the GTSP plant, such as the heat removed by cooling water in the cooler, based on unit product output, 538 KJ per lb of GTSP (Brown, et al., 1985). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 9 variables and 8 equations, so the number of degrees of freedom is 1. For the material and energy balance, there are 21 variables and 15 equations, so the number of degrees of freedom is 6.

Table 4-10 Constraint Equations for GTSP Production

Material Balance	
Overall	$(F_{12}+F_{39}+F_{74})-(F_{51}+F_{63}+F_{422})=0$ where $F_{12}=F_{12}^{(ROCK)}$ $F_{39}=F_{39}^{(P_2O_5)}+F_{39}^{(H_2O)}$
Species	P_2O_5: $\frac{UPAGTSP}{\frac{141.94}{(2)(98)}}F_{39}^{(P_2O_5)}-\frac{(PGTSP)(14)(98)}{\frac{141.94}{234.06}(10)(234.06)}F_{51}=0$ ROCK: $F_{12}^{(ROCK)}-\frac{(UPAGTSP)(2)(98)(1008.62)(100)(3)(310.18)}{(141.94)(14)(98)(BPLGTSP)(1008.62)(URGTSP)}F_{39}^{(P_2O_5)}=0$ HF: $\frac{(UPAGTSP)(2)(98)(2)(20.01)}{(141.94)(14)(98)}F_{39}^{(P_2O_5)}-F_{63}=0$ H_2O: $F_{422}-(F_{39}^{(H_2O)}-\frac{(3)(18.02)}{141.94}F_{39}^{(P_2O_5)})=0$
Energy Balance	
Overall	$((PGTSP)F_{51}^{(GTSP)}/M^{(P_2O_5)}H^{(GTSP)}+F_{63}^{(HF)}/M^{(HF)}H_{63}^{(HF)}+F_{422}^{(H_2O)}/M^{(H_2O)}H_{422}^{(H_2O)})$ $-((BPLGTSP)/(100)F_{12}^{(ROCK)}/((3)M^{(Ca_3(PO)_4)})H^{(ROCK)}+$ $\Sigma F_{39}^{(i)}/M^{(i)}H^{(i)})+F_{51}Q_{out}-Q_{GTSP}=0$ $i = P_2O_5, H_2O$
Enthalpy Function	$H_k^i(T)=(a_1^i+\frac{1}{2}a_2^iT+\frac{1}{3}a_3^iT^2+\frac{1}{4}a_4^iT^3+\frac{1}{5}a_5^iT^4+\frac{b_1^i}{T})RT$ J/mol $i = H_2O, HF$; $k = 39, 63, 422$ $H^{(ROCK)}(T)=(((-291.5)(1000)+(3)(-984.9)(1000))+(16.02+(3)(54.45))$ $(T-298.15))(4.182)J/mol$ Source: Lide (1982) $H^{(P_2O_5)}=(-1278.437)(1000)+(106.014)(T-298.15)J/mol$ Source: Lide (1982) $H^{(GTSP)}(T)=(-742.04)(1000)(4.182)+(246.4)(T-298.15)J/mol$ Source: Felder and Roussleu (1986)

B-4. Ammonia (Hertwig, 2004; Brykowski, 1981; Perry, 1997; Louisiana Chemical & Petroleum Products List, 1998)

In the chemical production complex in the lower Mississippi River corridor, the ammonia production plants are as follow (Louisiana Chemical & Petroleum Products List, 1998).

- IMC-Agrico, Faustina Plant (480 thousand metric tons per year)
- CF Industries, Donaldsonville (1.84 million metric tons per year)
- Triad Nitrogen, Donaldsonville (1.02 million metric tons per year)
- BCP, Geismar (400 thousand metric tons per year)
- PCS Nitrogen Fertilizer LP, Geismar (550 thousand metric tons per year)
- Monsanto, Luling (440 thousand metric tons per year)
- Cytec, Westwego (385 thousand metric tons per year)
- Air Product & Chemicals Inc., St. Gabriel (270 thousand metric tons per year)

For the ammonia production, the capacity of 1,986 tons per day was used in the base case (Hertwig, 2004).

B-4-1. Process Description

The block diagram for ammonia process is given in Figure 4.5 with the stream definitions in Table 4-11. After desulfurization the natural gas is fed to the primary reformer (steam reformer), where part of the methane is converted to carbon oxides and hydrogen over a nickel catalyst. Then the gas mixture enters the secondary reformer (autothermic reformer) where air is injected to provide nitrogen needed in ammonia synthesis. Because carbon oxides are highly poisonous to the ammonia synthesis catalyst, the reformed gas mixture is shifted for more H_2 and scrubbed for CO_2 removal, where carbon monoxide is oxidized to carbon dioxide. Then, in the methanator the remaining traces of CO_2 are removed by reaction with H_2 to produce methane and water. Finally, the synthesis gas is compressed and converted to ammonia in the synthesis reactor. More detail information about the plant is given below.

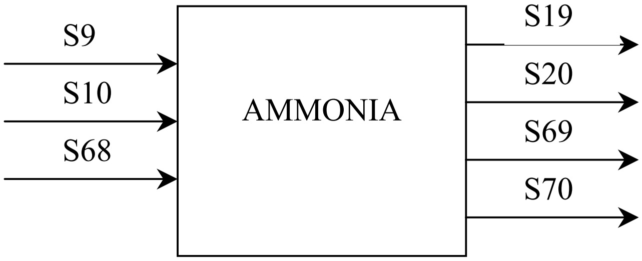


Figure 4.5 Block Diagram of Ammonia Plant

Table 4-11 Description of Process Streams in Ammonia Plant

Name of Streams	Description
Input Streams	
S9	Air to ammonia plant
S10	Natural gas to ammonia plant
S68	Steam (reactant) to ammonia plant
Output Streams	
S19	Total production of ammonia from ammonia plant
S20	Total production of CO_2 from ammonia plant
S69	Water from ammonia plant
S70	Purge from ammonia plant

B-4-1-1. Synthesis Gas Preparation

The steam reforming reaction is:

$$CH_4 + H_2O = CO + 3H_2 \tag{4-21}$$

The reaction is very endothermic, favored by high temperature and low pressure.

The water-gas shift reaction is employed to convert CO to CO_2 with additional H_2 production.

$$CO + H_2O = CO_2 + H_2 \qquad \Delta H(1000°C) = -32.18 \text{ MJ/Kgmol} \qquad (4\text{-}22)$$

The reaction is mildly exothermic, favored by low temperature and unaffected by pressure. When the final product is CO_2, excess steam is used to prevent carbon formation. In the NH_3 plant, this reaction occurs with the reforming in the primary reformer that operates at 760-980°C. Product composition depends on process conditions, such as temperature, pressure, excess steam which determines equilibrium, and velocity through the catalyst bed which determines approach to equilibrium. Typical product is 75% H_2, 8% CO, 15% CO_2, 2% balance gases of N_2 and CH_4. Additional cooling and steam is provided to finish converting CO to CO_2 in the shift converters (Equation 4-22). After the secondary reformer air is introduced to provide N_2 to form NH_3. Oxygen from the introduced air will complete the oxidation of any remaining CH_4 and CO (Equation 4-23 and 4-24). Oxidation product H_2O is condensed out, and oxidation product CO_2 is scrubbed out using amines.

$$CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O(g) \quad \Delta H(25^oC) = -191.759 \text{ Kcal/gmole} \quad (4\text{-}23)$$

$$CO + 0.5O_2 = CO_2 \qquad \Delta H(25^oC) = -67.6361 \text{ Kcal/gmole} \quad (4\text{-}24)$$

The trace of CO_2 left is converted back to CH_4 in a methanator (Equation 4-25).

$$CO_2 + 4H_2 = CH_4 + 2H_2O \qquad (4\text{-}25)$$

B-4-1-2. NH_3 Synthesis

The ammonia synthesis reaction is:

$$0.5N_2 + 1.5H_2 = NH_3 \qquad (4\text{-}26)$$

The converter consists of a high-pressure shell containing a catalyst section and a heat exchanger. Both horizontal and vertical types of converter are used with cooling by quenching. Inlet gases conventionally pass along the shell, being preheated and reducing the maximum shell temperature. The conditions in the converter are 500 ^{o}C and 15 to 30 MPa. Outlet concentrations of ammonia are 16 to 25%. Product can be liquid or gas. Liquification makes storage practical but requires energy and equipment to produce, and ammonia is usually re-vaporized in the customer's process. A trace of water is added to the NH_3 liquid product to control corrosion of carbon steel.

Steam demand within the NH_3 plant usually is a close match to the NH_3 plant's steam production. Extra steam can be produced within the NH_3 plant for users inside or outside the NH_3 plant by firing the auxiliary burners in the heat-recovery section of the exhaust gas from the primary reformer.

The biggest yield losses are due to the inerts purge: inerts include Ar from the air feed and CH_4 from the CO_2 Methanator. The purge is usually passed through a H_2-recovery unit (HRU). When the remaining purge contains enough CH_4 and H_2, it is sent to the primary reformer as a fuel.

B-4-2. Material Balance and Energy Balance

With the parameters shown in Table 4-12, the material and energy balances of the ammonia plant are given in Table 4-13.

In Table 4-13, the overall material balance for the whole process is given with the mixture stream expressions. For the species material balance obtained using the reaction equations (4-21,4-22, 4-23, 4-24, 4-25 and 4-26), the first equation is for the methane balance; the second one is for the steam used as a reactant balance; the third one is for the CO_2 balance; the fourth one is for the NH_3 balance; the fifth one is for the purge N_2 balance; the sixth one is for the purge H_2 balance; the seventh one is for the purge Ar balance; the last one is for the water balance.

Table 4-12 Parameters in Ammonia Production, from Hertwig (2004)

Name	Meaning	Value
UHAMM	Utilization of H_2 in ammonia plant(higher than N_2 utilization due to H_2 recovery unit)	0.999
UNAMM	Utilization of N_2 in ammonia plant	0.995
	Trace of water added to NH_3 product for corrosion control (not used in any calculation yet)	0.0
	Air composition:	
	N_2 in air	78.084%
	O_2 in air	20.946%
	Ar in air	0.934%
	CO_2 in air	0.036%

In the overall energy balance, Q_{AMM} is the heat from steam in the primary refomer for synthesis gas preparation (Equation 4-21), heat exchanger, and distillation column reboilers, which is calculated from the energy balance. $Q_{utilities}$ is the heat output removed by cooling water in heat exchanger and distillation column condensers during unit operations, such as methanation and ammonia separation, in the ammonia plant based on the unit of ammonia product, 3 MJ per lb of ammonia (Brykowski, 1981). Q_{purge} is the heat from the combustion of purge H_2 used as fuel gas, -54 MJ per lb of H_2 (Perry, 1997). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

Table 4-13 Constraint Equations for Ammonia Production

Material Balance	
Overall	$(F_9 + F_{10} + F_{68}) - (F_{19} + F_{20} + F_{69} + F_{70}) = 0$ where $F_9 = F_9^{(O_2)} + F_9^{(N_2)} + F_9^{(CO_2)} + F_9^{(Ar)}$ $F_{70} = F_{70}^{(N_2)} + F_{70}^{(H_2)} + F_{70}^{(Ar)}$
Species	CH_4: $F_{10} - \frac{(0.5)(0.20946)(16.05)}{(17.04)(0.78084)(2)(UNAMM)}F_{19} - \frac{(1.5)(16.05)}{(17.04)(4)(UHAMM)}F_{19} = 0$ Steam: $F_{68} - \frac{(1.5)(18.02)(2)}{(17.04)(4)(UHAMM)}F_{19} = 0$ CO_2: $F_9^{(CO_2)} + (\frac{(1.5)(44.01)}{(17.04)(4)(UHAMM)} + \frac{(0.5)(0.20946)(44.01)}{(17.04)(0.78084)(2)(UNAMM)})F_{19}$ $- F_{20} = 0$ NH_3: $\frac{(17.04)(UNAMM)}{(0.5)(28.02)}F_9^{(N_2)} - F_{19} = 0$ N_2 purge: $-F_{70}^{(N_2)} + \frac{(0.5)(28.02)(1-UNAMM)}{(17.04)(UNAMM)}F_{19} = 0$ H_2 purge: $-F_{70}^{(H_2)} + \frac{(1.5)(2.02)(1-UHAMM)}{(17.04)(UHAMM)}F_{19} = 0$ Ar purge: $F_9^{(Ar)} - F_{70}^{(Ar)} = 0$ H_2O: $-F_{69} + \frac{(0.5)(0.20946)(2)(18.02)}{(17.04)(0.78084)(2)(UNAMM)}F_{19} = 0$
Energy Balance	
Overall	$(F_{19}^{(NH_3)} / M^{(NH_3)}H_{19}^{(NH_3)} + F_{20}^{(CO_2)} / M^{(CO_2)}H_{20}^{(CO_2)} + \Sigma F_{70}^{(j)} / M^{(j)}H_{70}^{ji)}$ $+ F_{69}^{(H_2O)} / M^{(H_2O)}H_{69}^{(H_2O)}) - (F_{10}^{(CH_4)} / M^{(CH_4)}H_{10}^{(CH_4)} + \Sigma F_9^{(i)} / M^{(i)}H_9^{(i)}$ $+ F_{68}^{(H_2O)} / M^{(H_2O)}H_{68}^{(H_2O)}) + F_{19}^{(NH_3)}Q_{utilities} + F_{70}^{(H_2)}Q_{purge} - Q_{AMM} = 0$ i = CO_2, O_2, N_2, Ar; j = H_2, N_2, Ar
Enthalpy Function	$H_k^i(T) = (a_1^i + \frac{1}{2}a_2^iT + \frac{1}{3}a_3^iT^2 + \frac{1}{4}a_4^iT^3 + \frac{1}{5}a_5^iT^4 + \frac{b_1^i}{T})RT$ J/mol i = H_2O, CO_2, CH_4, O_2, N_2, Ar, NH_3 k = 9, 10, 19, 20, 68, 69, 70

In the material balance part, there are 14 variables and 14 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 34 variables and 27 equations including the dependent overall material balance, so the number of degrees of freedom is 8.

B-5. Nitric Acid (Hertwig, 2004; Keleti, 1985; Louisiana Chemical & Petroleum Products List, 1998)

In the chemical production complex in the lower Mississippi River corridor, the nitric acid plants are as follow (Louisiana Chemical & Petroleum Products List, 1986).

- CF industries, Donaldsonville (380 thousand tons per year)
- PCS Nitrogen Fertilizer LP, Geismar (923 thousand tons per year)
- Rubicon, Geismar (120 thousand tons per year)

For nitric acid production, the capacity of 539 tons per day was used in the base case (Hertwig, 2004).

B-5-1. Process Description

The reaction can be expressed as:

$$NH_3\ (g) + 2O_2\ (g) = HNO_3\ (aq) + H_2O\ (l) \qquad (4\text{-}27)$$

Commercial grades of the product range 0.534-0.687 w/w (36-42^{o}Be). The product concentrating to 0.95 is possible with additional processing cost for extractive distillation with a dehydrating agent as H_2SO_4 with $MgSO_4$. Manufactured acid contains some HNO_2 when 0.20-0.45 HNO_3 and contains dissolved N_2O_4 when greater than 0.55 HNO_3.

Atmospheric-pressure plants have been replaced by pressurized plants to reduce plant size and capital cost, and to be able to produce more than 0.50-0.55

HNO_3. Single-pressure/American/DuPont plants have lower capital cost and produce more by-product steam than dual-pressure/European plants that have lower catalyst cost and slightly higher yield. But overall costs are roughly similar for single- vs dual-pressure processes.

A block process diagram is given in Figure 4.6 with the stream definitions from Table 4-14. In order to get to the production grade and reduce operating cost, the water from ammonium nitrate plant is used.

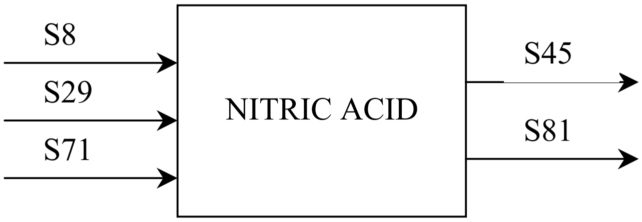


Figure 4.6 Block Diagram of Nitric Acid Plant

Table 4-14 Description of Process Streams in Nitric Acid Plant

Name of Streams	Description
Input Streams	
S8	Air to nitric acid plant
S29	Ammonia to nitric acid plant
S71	Water from ammonium nitrate plant to nitric acid plant
Output Streams	
S45	Nitric acid solution produced from nitric acid plant
S81	Vent gases from nitric acid plant

B-5-2. Material Balance and Energy Balance

Using the parameters in Table 4-15, the material balance and energy balance of nitric acid plant are given in Table 4-16.

In Table 4-16, the overall material balance for the whole process is given with the mixture stream expressions. For the species material balance obtained using the reaction equations (4-27), the first equation is for the O_2 (reactant) balance; the second one is for the NH_3 balance; the third one is for the H_2O balance; the fourth one is for the O_2 (inert) balance; the fifth one is for the N_2 balance; the sixth one is for the CO_2 balance; the seventh one is for the Ar balance; the last one is for the NO balance.

Table 4-15 Parameters in Nitric Acid Production, from Hertwig (2004)

Name	Meaning	Value
CONCNA	Product nitric acid concentration (0.54-0.68) (weight fraction)	0.54
ABNOL	NO absorption	0.980
	Weight fraction of the air required to "bleach" red NO_2 out of product HNO_3 in the total air input	0.15

In the overall energy balance, Q_{NIT} is the net heat released from the nitric acid plant in the form of steam in the heat exchanger because of the exothermic reaction (4-27), which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in the heat exchanger and absorption column in the nitric acid plant based on the unit of nitric acid product, 1 MJ per lb of nitric acid (100%) (Keleti, 1985). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 16 variables and 16 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 35 variables and 30 equations including the dependent overall material balance, so the number of degrees of freedom is 6.

Table 4-16 Constraint Equations for Nitric Acid Production

Material Balance	
overall	$(F_8 + F_{29} + F_{71}) - (F_{45} + F_{81}) = 0$ where $F_8 = F_8^{(O_2)} + F_8^{(N_2)} + F_8^{(CO_2)} + F_8^{(Ar)}$ $F_{45} = F_{45}^{(HNO_3)} + F_{45}^{(H_2O)}$ $F_{81} = F_{81}^{(O_2)} + F_{81}^{(N_2)} + F_{81}^{(Ar)} + F_{81}^{(CO_2)} + F_{81}^{(NO)}$
species	O_2: $F_8^{(O_2)} - F_{81}^{(O_2)} - \frac{(2)(32)}{63.02}F_{45}^{(HNO_3)} - \frac{(5)(32)}{(30.01)(4)}F_{81}^{(NO)} = 0$ NH_3: $F_{29} - \frac{17.04}{63.02}F_{45}^{(HNO_3)} - \frac{17.04}{30.01}F_{81}^{(NO)} = 0$ H_2O: $F_{71} + \frac{18.02}{63.02}F_{45}^{(HNO_3)} + \frac{(6)(18.02)}{(30.01)(4)}F_{81}^{(NO)} - F_{45}^{(H_2O)} = 0$ O_2: $F_{81}^{(O_2)} - 0.15F_8^{(O_2)} = 0$ N_2: $F_{81}^{(N_2)} - F_8^{(N_2)} = 0$ CO_2: $F_{81}^{(CO_2)} - F_8^{(CO_2)} = 0$ Ar: $F_{81}^{(Ar)} - F_8^{(Ar)} = 0$ NO: $\frac{1}{30.01}F_{81}^{(NO)} - \frac{1-ABNOL}{17.04}F_{29} = 0$
Energy Balance	
Overall	$(\Sigma F_{45}^{(i)}/M^{(i)}H_{45}^{(i)} + \Sigma F_{81}^{(j)}/M^{(j)}H_{81}^{(j)}) - (F_{29}^{(NH_3)}/M^{(NH_3)}H_{29}^{(NH_3)} +$ $F_{71}/M^{(H_2O)}H_{71} + \Sigma F_8^{(k)}/M^{(k)}H_8^{(k)}) + F_{45}^{(HNO_3)}Q_{out} - Q_{NIT} = 0$ i = HNO_3, H_2O; j = CO_2, O_2, N_2, Ar, NO; k = CO_2, O_2, N_2, Ar
Enthalpy Function	$H_k^i(T) = (a_1^i + \frac{1}{2}a_2^iT + \frac{1}{3}a_3^iT^2 + \frac{1}{4}a_4^iT^3 + \frac{1}{5}a_5^iT^4 + \frac{b_1^i}{T})RT$ J/mol i = H_2O, CO_2, O_2, N_2, Ar, NH_3, NO k = 8, 29, 45, 71, 81 $H_k^{(HNO_3)}(T) = (-174.1)(1000) + (109.9)(T - 298.15)J/mol$ k=45 Source: Knovel (2003)

B-6. Urea (NH_2CONH_2) (Hertwig, 2004; Austin, 1984; Meyers, 1986; Louisiana Chemical & Petroleum Products List, 1998)

In the chemical production complex in the lower Mississippi River corridor, the urea plants are as follow (Louisiana Chemical & Petroleum Products List, 1998).

- IMC-Agrico, Faustina Plant (260 thousand tons per year)
- CF Industries, Donaldsonville (1.6 million tons per year)
- BCP, Geismar (220 thousand tons per year)
- PCS Nitrogen Fertilizer LP, Geismar (412 thousand tons per year)
- Cytec Industries, Westwego (120 thousand tons per year)
- Triad Nitrogen, Donaldsonville (420 thousand tons per year)

For urea production, the capacity of 301 tons per day was used for the base case (Hertwig, 2004).

B-6-1. Process Description

There are two reaction steps (4-28 and 4-29) in the urea production. Usually, these two reactions can be expressed as overall reaction (4-30).

$$CO_2 + 2NH_3 = NH_2COONH_4 \qquad \Delta H = -155 \text{ MJ/Kgmol} \qquad (4\text{-}28)$$

$$NH_2COONH_4 = NH_2CONH_2 + H_2O \qquad \Delta H = +42 \text{ MJ/Kgmol} \qquad (4\text{-}29)$$

$$CO_2 + 2NH_3 = NH_2CONH_2 + H_2O \qquad (4\text{-}30)$$

Both (4-28) and (4-29) are equilibrium reactions. Carbamate (NH_2COONH_4) formation in Equation 4-28 goes to completion at 14 MPa and 170-190^oC. Most of heat of reaction (4-28) goes into steam production.

Decomposition to urea (NH_2CONH_2) in Equation 4-29 is slow. It is less complete and driven by heat and pressure reduction. This is done in one or more decomposers at progressively lower pressures. Decomposer product is a urea solution that must be evaporated to be prilled or granulated. Heating the solution with the low pressure steam (LP) releases unreacted gases and undecomposes carbamate and evaporates water. Part of this heat comes from the heat of forming the carbamate.

Conversion of either reactant is helped by using an excess of the other reactants (NH_3 and CO_2). However, the theoretical amount of CO_2 is employed to make the material balance simple. Unconverted CO_2, NH_3 and undecomposed carbamate are recovered and recycled. This requires that all of the evolved gases must be repressurized to reactor pressure. Synthesis is further complicated by formation of a dimmer called biuret, $NH_2CONHCONH_2 \cdot 2H_2O$, which is toxic to many plant species at high concentrations. Biuret in urea can cause agronomic problems if placed near the seed. The major damage of biuret is to germinating seeds. Although some crops have been affected, there is little damage through plant absorption. So biuret content is typically around 0.3%. Overall, over 99% of both CO_2 and NH_3 are converted to urea, making environmental problems minimal. Air is introduced into the process with the CO_2 to provide O_2 to let 300 series stainless steels resist carbamate that is otherwise very corrosive to ordinary and stainless steels.

The block diagram is given in Figure 4.7 with the stream definitions from Table 4-17. CO_2 and NH_3 both come from an ammonia plant. NH_3 feed is as a gas for urea production in the chemical production complex. NH_3 can be liquid (Austin, 1984). Urea product is relatively pure. Product of 46% N used to be prilled but today it is usually granulated. Additives can slow storage decomposition losses to CO_2 and NH_3 that occurs over several months. Urea solutions are sometimes sold.

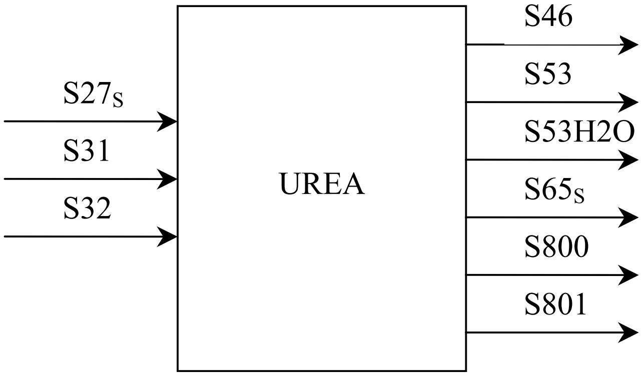


Figure 4.7 Block Diagram of Urea Plant

Table 4-17 Description of Process Streams in Urea Plant

Name of Streams	Description
Input Streams	
$S27_S$	LP steam to urea plant for heat exchange
S31	Ammonia to urea plant
S32	CO_2 to urea plant
Output Streams	
S46	Granular urea produced from urea plant
S53	Urea solid produced from urea plant for DAP N% control
S53H2O	Water produced from urea plant
$S65_S$	Condensed water from LP input in urea plant
S800	NH_3 emission from urea plant
S801	CO_2 emission from urea plant

B-6-2. Material Balance and Energy Balance

Using the parameters in Table 4-18, the material balance and energy balance of the urea plant are given in Table 4-19.

Table 4-18 Parameters in Urea Production, from Hertwig (2004)

Name	Meaning	Value
UAMMUR	NH_3 utilization in urea plant	0.999
UCO2UR	CO_2 utilization in urea plant	0.999

In Table 4-19, the overall material balance for the whole process is given with the heat exchange balance and mixture stream expressions. For the species material balance obtained using the reaction equations (4-28, 4-29 and 4-30), the first equation is for the water balance; the second one is for the total NH_3 balance; the third one is for the NH_3 emission balance; the fourth one is for the CO_2 emission balance; the fifth one is for the total CO_2 balance; the last one is for the urea balance.

Table 4-19 Constraint Equations for Urea Production

Material Balance	
Overall	$(F_{S27}+F_{31}+F_{32})-(F_{46}+F_{53}+F_{53}^{(H_2O)}+F_{S65}+F_{800}+F_{801})=0$ where $F_{53}=F_{53}^{(UREA)}$ Heat exchange: $F_{S27}-F_{S65}=0$
Species	H_2O: $\frac{1}{EEVAUR}F_{53}^{(H_2O)}-F_{S27}=0$ NH_3: $F_{31}-\frac{(17.04)(2)}{(60.07)(UAMMUR)}(F_{53}^{(UREA)}+F_{46})=0$ NH_3 emission: $-F_{800}+\frac{(17.04)(2)(1-UAMMUR)}{(60.07)(UAMMUR)}(F_{53}^{(UREA)}+F_{46})=0$ CO_2 emission: $-F_{801}+\frac{(44.01)(1-UCO2UR)}{(60.07)(UCO2UR)}(F_{53}^{(UREA)}+F_{46})=0$ CO_2: $F_{32}-\frac{44.01}{(60.07)(UCO2UR)}(F_{53}^{(UREA)}+F_{46})=0$ Urea: $\frac{18.02}{60.07}(F_{53}^{(UREA)}+F_{46})-F_{53}^{(H_2O)}=0$
Energy Balance	
Overall	$(F_{53}^{(UREA)}/M^{(UREA)}H_{53}^{(UREA)}+F_{53}^{(H_2O)}/M^{(H_2O)}H_{53}^{(H_2O)}+F_{46}^{(UREA)}$ $/M^{(UREA)}H_{46}^{(UREA)}+F_{800}^{(NH_3)}/M^{(NH_3)}H_{800}^{(NH_3)}+F_{801}^{(CO_2)}/M^{(CO_2)}H_{801}^{(CO_2)})$ $-(F_{31}^{(NH_3)}/M^{(NH_3)}H_{31}^{(NH_3)}+F_{32}^{(CO_2)}/M^{(CO_2)}H_{32}^{(CO_2)})+Q_{out}(F_{53}^{(UREA)}+F_{46})$ $-Q_U=0$
Enthalpy Function	$H_k^i(T)=(a_1^i+\frac{1}{2}a_2^iT+\frac{1}{3}a_3^iT^2+\frac{1}{4}a_4^iT^3+\frac{1}{5}a_5^iT^4+\frac{b_1^i}{T})RT$ J/mol i = H_2O, CO_2, NH_3 k = 31, 32, 53H_2O, 800, 801 $H_k^{(UREA)}(T)=(-333.6)(1000)+(93.14)(T-298.15)J/mol$ k=46, 53 Source: Domalski, et al. (1984)

In the overall energy balance, Q_U is the heat input of the plant in the form of steam for heat for the reaction (Equation 4-29) and in the heat exchanger, and one-stage evaporator and vacuum evaporator, which is calculated from the energy balance. The reaction heat from Equation 4-28 is not enough for the total heat requirements of the plant. Q_{out} is the heat output removed by cooling water in the heat exchanger, scrubber, condenser and stripper in the urea plant based on the unit of urea product, 1.6 MJ per lb of urea (Meyers, 1986). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 10 variables and 9 equations including one dependent equation (overall mass balance), so the number of degrees of freedom is 2. For the material and energy balance, there are 24 variables and 17 equations including the dependent overall mass balance, so the number of degrees of freedom is 8.

B-7. Methanol (CH_3OH or MeOH) (Hertwig, 2004; Brown, et al., 1985; Louisiana Chemical & Petroleum Products List, 1998)

In the chemical production complex in the lower Mississippi River corridor, the methanol plants are given as follow (Louisiana Chemical & Petroleum Products List, 1998).

- BCP, Geismar (330 million gallons per year)
- Ashland, Plaquemine (160 million gallons per year)
- Cytec, Westwego (Not available)
- Georgia Gulf, Plaquemine (160 million gallons per year)
- Praxair, Geisamr (10 million gallons per year)

For methanol production, the capacity of 548 tons per day was used in the base case (Hertwig, 2004).

B-7-1. Process Description

The block flow diagram is given in Figure 4.8 with stream definitions from Table 4-20 and the detailed process description is given below.

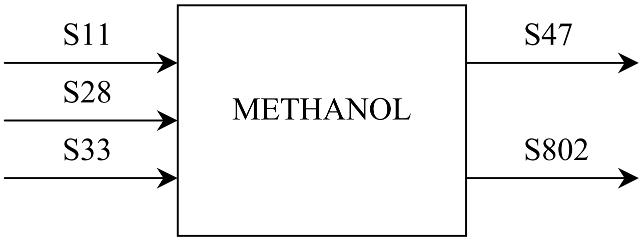


Figure 4.8 Block Diagram of Methanol Plant

Table 4-20 Description of Process Streams in Methanol Plant

Name of Streams	Description
Input Steams	
S11	Natural gas to methanol plant
S28	Steam to methanol plant
S33	CO_2 to methanol plant
Output Streams	
S47	Methanol produced from methanol plant
S802	Purge from methanol plant

B-7-1-1. Synthesis Gas Preparation

The steam reforming reaction is:

$$CH_4 + H_2O = CO + 3H_2 \tag{4-21}$$

The reaction is very endothermic, favored by high temperature and low pressure. This reaction produces 1:3 CO/H_2 instead of the 1:2 needed for MeOH synthesis, so another source of CO or CO_2 must be added. So CO_2 is imported in the MeOH plant instead of partial oxidation of CH_4 (4-31), which would supply CO, but with N_2 as an inert to this process.

$$CH_4 + 1.5O_2 = CO + 2H_2O \tag{4-31}$$

CO_2 is imported and in water-gas shift reaction (4-32), CO_2 is shifted back to CO by consuming some of the H_2 produced from CH_4 (4-21). The general reaction equation based on 4-21 and 4-32 of the synthesis gas preparation for methanol production using CH_4 and CO_2 as feedstock is Equation 4-33. The CO_2-to-CH_4 molar feeds ratio needs to be 1:3 to get 1:2 CO-to-H_2 for MeOH synthesis, though any incomplete conversion of CO_2 would call for a slightly higher feeds ratio. CO_2 conversion is hurt by the steam that is essential to H_2 generation. So careful control of steam-to-carbon ratio is needed to minimize CO_2 requirements. The stoichiometric molar ratio is 2:3 as calculated above. Unconverted CO_2 will waste CO_2 feed and carry MeOH, for example, with it when it has to be purged from the synthesis loop. Purge stream goes to the reformer to be burned as additional fuel.

$$CO_2 + H_2 = CO + H_2O \tag{4-32}$$

$$3CH_4 + 2H_2O + CO_2 = 4CO + 8H_2 \tag{4-33}$$

B-7-1-2. MeOH Synthesis in Catalytic Converter

$$CO + 2H_2 = CH_3OH \qquad \Delta H = -103 \text{ MJ/ Kgmol} \tag{4-34}$$

The converter in the Lurgi LP plant is a cooled multi-tubular reactor running at 5-8MPa and 250-260 ^{o}C. Liquid-entrained micron-sized copper-based catalysts can convert as much as 25% per pass (Equation 4-34). The heat of reaction is directly used to generate high pressure steam. MeOH is condensed by both heat exchange and pressure reduction. Condensed MeOH is collected and purified. Steam demand within the MeOH plant usually is a close match to the MeOH plant's steam production. Extra steam can be produced within the MeOH plant for users inside or outside the MeOH plant by firing the auxiliary burners in the heat-recovery section of the exhaust gas from the primary reformer.

B-7-2. Material Balance and Energy Balance

Using the parameters in Table 4-21, the material balance and energy balance of methanol plant are given in Table 4-22.

Table 4-21 Parameters in Methanol Production, from Hertwig (2004)

Name	Meaning	Value
UH2ME	Overall H_2 utilization in methanol plant	0.999
UCO2ME	Overall CO_2 utilization in methanol plant	0.99

In Table 4-22, the overall material balance for the whole process is given with the mixture stream expressions. For the species material balance obtained using the reaction equations (4-33 and 4-34), the first equation is for the CO_2 (reactant) balance; the second one is for the CH_4 balance; the third one is for the H_2O balance; the fourth one is for the purged H_2 balance; the fifth one is for the purged CO_2 (inert) balance; the last one is for the purged CO balance.

In the overall energy balance, Q_{MET} is heat input of the methanol plant in the form of steam in the heat exchanger and methanol separation units, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in heat exchanger, cooler, condenser and methanol separation unit, based on the unit of methanol product, 4.6 MJ per lb of methanol (Brown, et al., 1985). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

Table 4-22 Constraint Equations for Methanol Production

Material Balance	
Overall	$(F_{11} + F_{28} + F_{33}) - (F_{47} + F_{802}) = 0$
	where $F_{802} = F_{802}^{(H_2)} + F_{802}^{(CO_2)} + F_{802}^{(CO)}$
Species	CO_2: $F_{33} - \frac{44.01}{(4)(32.05)(UCO2ME)} F_{47} = 0$
	CH_4: $F_{11} - \frac{(3)(16.05)}{(4)(32.05)(UH2ME)} F_{47} = 0$
	H_2O: $F_{28} - \frac{18.02}{16.05} F_{11} + \frac{(18.02)(UCO2ME)}{44.01} F_{33} = 0$
	H_2 purge: $-F_{802}^{(H_2)} + \frac{(1-UH2ME)(3)(2.02)}{16.05} F_{11} = 0$
	CO_2 purge: $-F_{802}^{(CO_2)} + (1-UCO2ME)F_{33} = 0$
	CO purge: $-F_{802}^{(CO)} + \frac{(1-UH2ME)(28.01)}{16.05} F_{11} = 0$
Energy Balance	
Overall	$F_{47}^{(MeOH)} / M^{(MeOH)} H_{47}^{(MeOH)} + \Sigma F_{802}^{(i)} / M^{(i)} H_{802}^{(i)} - (F_{11}^{(CH_4)} / M^{(CH_4)} H_{11}^{(CH_4)} +$
	$F_{28}^{(H_2O)} / M^{(H_2O)} H_{28}^{(H_2O)} + F_{33}^{(CO_2)} / M^{(CO_2)} H_{33}^{(CO_2)})$
	$+ Q_{out} F_{47} - Q_{MET} = 0$
	$i = CO_2, CO, H_2$
Enthalpy Function	$H_k^i(T) = (a_1^i + \frac{1}{2} a_2^i T + \frac{1}{3} a_3^i T^2 + \frac{1}{4} a_4^i T^3 + \frac{1}{5} a_5^i T^4 + \frac{b_1^i}{T}) RT$ J/mol
	$i = CO_2, CH_4, H_2O, CO, H_2$
	$k = 11, 28, 33, 802$
	$H_k^{(MeOH)}(T) = (-238.54)(1000) + (79.225)(T - 298.15)$ J/mol k=47
	Source: Felder and Roussleu (1986)

In the material balance part, there are 8 variables and 8 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 21 variables and 16 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 6.

B-8. Ammonium Nitrate ($AmNO_3$ or NH_4NO_3) (Hertwig, 2004; Search and Reznik, 1977; Louisiana Chemical & Petroleum Products List, 1998)

In the chemical production complex in the lower Mississippi River corridor, ammonium nitrate is produced by the following plants (Louisiana Chemical & Petroleum Products List, 1998).

- PCS Nitrogen, Geimar (485 thousand metric tons per year)
- CF Industries, Donaldsonville (340 thousand metric tons)

For ammnium nitrate production, the capacity of 684 tons per day was used for the base case (Hertwig, 2004).

B-8-1. Process Description

$$NH_3\ (g) + HNO_3\ (aq.) = NH_4NO_3\ (aq.) \qquad \Delta H = -86.2\ kJ / gmol \quad (4\text{-}35)$$

Ammonium nitrate is made by reacting nitric acid with ammonia (4-35). Both feeds are preheated and product is air-cooled. If feeds are properly heated and proportioned, the heat of reaction finishes drying the product. Continuous processes are employed instead of batch processes because of the labor and equipment costs. Figure 4.9 shows a block diagram with the stream definitions in Table 4-23.

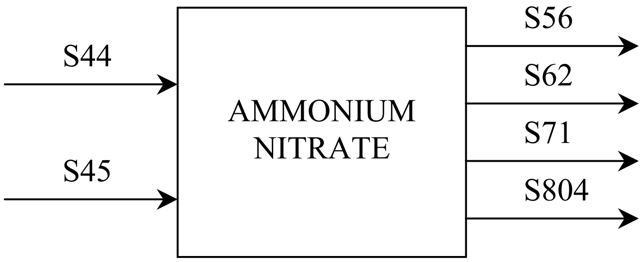


Figure 4.9 Block Diagram of Ammonium Nitrate Plant

Table 4-23 Description of Process Streams in Ammonium Nitrate Plant

Name of Streams	Description
Input Streams	
S44	Ammonia to ammonium nitrate plant
S45	Nitric acid solution to ammonium nitrate plant
Output Streams	
S56	Granular ammonium nitrate from ammonium nitrate plant
S62	Ammonium nitrate solution from ammonium nitrate plant
S71	Water from ammonium nitrate plant to nitric acid plant
S804	Water from ammonium nitrate plant but not to nitric acid plant

B-8-2. Material Balance and Energy Balance

Using the parameters in Table 4-24, the material balance and energy balance of the ammonium nitrate plant are given in Table 4-25. In Table 4-25, the overall material balance for the whole process is given with the mixture stream expressions. For the species material balance obtained using the reaction equations (4-35), the first equation is for the HNO_3 balance; the second one is for the NH_3 balance; the last one is for the H_2O balance.

In the overall energy balance, Q_{AN} is heat input of the ammonium nitrate plant in the form of steam in the heat exchanger and preheater, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water and the air for cooling in the prilling tower and cooler in ammonium nitrate plant, based on the unit of ammonium nitrate product, 62 KJ per lb of ammonium nitrate (Search and Reznik, 1977). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 10 variables and 8 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 3. For the material and energy balance, there are 25 variables and 17 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 9.

Table 4-24 Parameters in Ammonium Nitrate Production, from Hertwig (2004)

Name	Meaning	Value
UAMMAMN	NH_3 utilization in ammonium nitrate plant	1.0
UNITAMN	HNO_3 utilization in ammonium nitrate plant	1.0
CONCAMN	Concentration of ammonium nitrate solution product	0.30

Table 4-25 Constraint Equations for Ammonium Nitrate Production

Material Balance	
Overall	$(F_{44}+F_{45})-(F_{56}+F_{62}+F_{71}+F_{804})=0$ where $F_{45}=F_{45}^{(HNO_3)}+F_{45}^{(H_2O)}$ $F_{62}=F_{62}^{(AN)}+F_{62}^{(H_2O)}$
Species	HNO_3: $F_{45}^{(HNO_3)}-\frac{63.02}{80.06}(F_{62}^{(AN)}+F_{56})=0$ NH_3: $F_{44}-\frac{17.04}{80.06}(F_{62}^{(AN)}+F_{56})=0$ H_2O: $F_{45}^{(H_2O)}-F_{71}-F_{62}^{(H_2O)}-F_{804}=0$
Energy Balance	
Overall	$(F_{56}^{(AN)}/M^{(AN)}H_{56}^{(AN)}+\Sigma F_{62}^{(i)}/M^{(i)}H_{62}^{(i)}+F_{71}^{(H_2O)}/M^{(H_2O)}H_{71}^{(H_2O)}+$ $F_{804}^{(H_2O)}/M^{(H_2O)}H_{804}^{(H_2O)})-(F_{44}^{(NH_3)}/M^{(NH_3)}H_{44}^{(NH_3)}+\Sigma F_{45}^{(j)}/M^{(j)}H_{45}^{(j)})$ $+Q_{out}F_{56}^{(AN)}-Q_{AN}=0$ i = H_2O, AN; j = HNO_3, H_2O
Enthalpy Function	$H_k^i(T)=(a_1^i+\frac{1}{2}a_2^iT+\frac{1}{3}a_3^iT^2+\frac{1}{4}a_4^iT^3+\frac{1}{5}a_5^iT^4+\frac{b_1^i}{T})RT$ J/mol i = NH_3, HNO_3, H_2O k = 44, 45, 62, 71, 804 $H_k^{(AN)}(T)=(-365.381)(1000)+(139.261)(T-298.15)$ J/mol k=56, 62 Source: Lide (1982)

B-9. Mono-/Di-Ammonium Phosphates (MAP/DAP) (Hertwig, 2004; Brown, et al., 1985; Louisiana Chemical & Petroleum Products List, 1998)

In the chemical production complex in the lower Mississippi River corridor, MAP and DAP are produced by the following plants (Louisiana Chemical & Petroleum Products List, 1998).

- IMC-Agrico, Faustina (Not available)
- IMC-Agrico, Taft (600 thousand tons per year for DAP)
- Avondale Ammonia, Westwego (125 thousand metric tons per year for DAP)

For the chemical production, the capacities of 885 tons per day for MAP and 5,666 tons per day for DAP were used for the base case (Hertwig, 2004).

B-9-1. Process Description

The standard grades for ammonium phosphate fertilizers are listed in Table 4-26. The product grades for MAP and DAP are set as 11-52-0 and 18-46-0 in Table 4-26, respectively.

Table 4-26 Ammonium Phosphate Standard Grades

%N - %P_2O_5 - %K_2O	N/P Mole Ratio
18-46-0	1.73 (if a true "di-" is 2.00)
10-50-0	0.90
10-52-0	0.85
11-52-0	0.94

The process feeds include anhydrous NH_3 as vapor, phosphoric acid at 40-54% P_2O_5, water for scrubber, and N boosters, such as NH_2CONH_2 (granular or solution), NH_4NO_3 (granular or solution), and $(NH_4)_2SO_4$ which comes from the reaction of NH_3 and feed H_2SO_4 in the granulator.

The overall reactions are:

$$H_3PO_4 + NH_3 = NH_4H_2PO_4 \qquad \text{MAP} \qquad (4\text{-}36)$$

$$NH_4H_2PO_4 + NH_3 = (NH_4)_2HPO_4 \qquad \text{DAP} \qquad (4\text{-}37)$$

The block diagram is illustrated in Figure 4.10 with the stream definitions in Table 4-27. Ammonia and phosphoric acid are metered continuously to an agitated atmospheric tank (pre-neutralizer) in specific mole ratios to produce a liquid product. The liquid product, more NH_3, N-boosters, and recycled product fines are fed in specific mole ratios to a granulator to grow the fines into product granules. By adjusting feeds mole ratios and the N-boosters, different products of MAP and DAP can be manufactured. Granulator product is dried, cooled and screened. Screen fines and coarse material that get ground are each recycled to the granulator. Storage is indoors with big piles in a warehouse. Most products are shipped by barge and ship. Only small amounts get bagged for residential use.

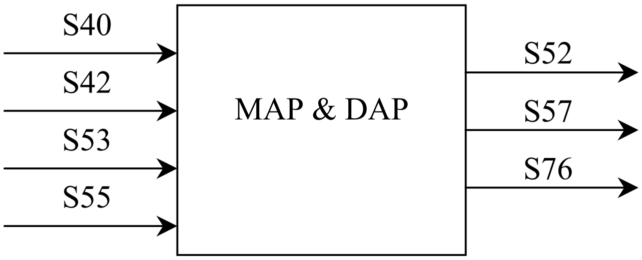


Figure 4.10 Block Diagram of MAP and DAP Plant

To control emissions of unreacted NH_3 and fluorides and of product dust, air is drawn through process vessels and scrubbed. By controlling H_3PO_4 additions, scrubber liquor pH is carefully controlled to be able to scrub both NH_3 and fluorides by Equation 4-38, 4-39, and 4-40. Permit limits apply though it is not yet feasible to measure these emissions on a continuous basis. Besides being a yield loss, emissions can cause NH_3-smell complaints from plant neighbors and formation of $(NH_4)_2SO_3$, a white haze, if NH_3 meets the trace amount of SO_2 from sulfuric plant stacks.

$$H_3PO_4 + NH_3 = NH_4H_2PO_4 \qquad \text{capture } NH_3 \qquad (4\text{-}38)$$

$$NH_3 + HF = NH_4F \qquad \text{capture HF} \qquad (4\text{-}39)$$

$$4NH_3 + 3SiF_4 + 2H_2O = 2(NH_4)_2SiF_6 + SiO_2 \qquad \text{capture } SiF_4 \qquad (4\text{-}40)$$

Table 4-27 Description of Process Streams in MAP and DAP Plant

Name of Streams	Description
Input Streams	
S40	Wet process phosphoric acid to MAP and DAP plant
S42	Ammonia to MAP and DAP plant
S53	Urea produced from urea plant as N-boosters to MAP and DAP plant
S55	Inert materials to MAP and DAP plant
Output Streams	
S52	MAP produced from MAP and DAP plant
S57	DAP produced from MAP and DAP plant
S76	Water vapor from MAP and DAP plant

B-9-2. Material Balance and Energy Balance

Using the parameters in Table 4-28 the material balance and energy balance of MAP and DAP plant are given in Table 4-29. In Table 4-29, the overall material balance for the whole process is given with the mixture stream expressions. For the species material balance obtained using the reaction equations (4-36 and 4-37), the first equation is for the P_2O_5 balance; the second one is for the NH_3 balance; the third one is for the urea (N-boosters) balance; the fourth one is for the water balance; the last one is for the MAP balance.

In the overall energy balance, Q_{APG} is heat input to MAP and DAP plant from steam in the heat exchangers and dryer, and it is calculated from the energy balance.

Q_{out} is the heat output from reaction heat removed by cooling water in the heat exchanger with the reactor in MAP and DAP plant based on the unit of MAP and DAP product, 402 KJ per lb of MAP and DAP (Brown, et al., 1985). Since the overall energy balance is based on Equation 4-36 and 4-37, and urea as the N-booster is not in these reactions, urea and the inert impurities are not considered in energy balance, just the balance from the reaction equation directly is evaluated. In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 9 variables and 8 equations, so the number of degrees of freedom is 1. For the material and energy balance, there are 21 variables and 15 equations, so the number of degrees of freedom is 6.

Table 4-28 Parameters in MAP and DAP Production, from Hertwig (2004)

Name	Meaning	Value
NMAP	% content of N in MAP	11
P2O5MAP	% content of P_2O_5 in MAP	52
NDAP	% content of N in DAP	18
P2O5DAP	% content of P_2O_5 in DAP	46
RPDAP	Ratio of P_2O_5 to DAP	0.68
RPMAP	Ratio of P_2O_5 to MAP	0.12
UPAGTSP	P_2O_5 utilization in ammoniation	0.999
NBRDAP	N-booster addition rate(urea solution) (T 100%-basis urea per T of DAP)	0.01362
PURMAP	Purity of $NH_4H_2PO_4$ in MAP	0.6357
PURDAP	Purity of $(NH_4)_2HPO_4$ in DAP (contains some MAP)	0.7705

B-10. Urea Ammonium Nitrate Solution (UAN) (Hertwig, 2004; Louisiana Chemical & Petroleum Products List, 1998)

In the chemical production complex in the lower Mississippi River corridor, UAN is produced by the following plants (Louisiana Chemical & Petroleum Products

Table 4-29 Constraint Equations for MAP and DAP Production

Material Balance	
Overall	$(F_{40}+F_{42}+F_{53}+F_{55})-(F_{52}+F_{57}+F_{76})=0$ where $F_{40}=F_{40}^{(P_2O_5)}+F_{40}^{(H_2O)}$ $F_{53}=F_{53}^{(UREA)}$
Species	P_2O_5: $F_{40}^{(P_2O_5)}-(\frac{P2O5MAP}{100}F_{52}+\frac{P2O5DAP}{100}F_{57})=0$ NH_3: $\frac{1}{17.04}F_{42}-\frac{(RPDAP)(NDAP)}{(RPDAP+RPMAP)(P2O5DAP)(14.01)}F_{40}^{(P_2O_5)}$ $-\frac{(RPMAP)(NMAP)}{(RPDAP+RPMAP)(P2O5MAP)(14.01)}F_{40}^{(P_2O_5)}=0$ UREA: $F_{53}^{(UREA)}-(NBRDAP)F_{57}=0$ H_2O: $F_{76}-(F_{40}^{(H_2O)}-\frac{(3)(18.02)}{141.94}F_{40}^{(P_2O_5)})=0$ MAP: $F_{52}-\frac{(RPMAP)(100)}{(RPDAP+RPMAP)(P2O5MAP)}F_{40}^{(P_2O_5)}=0$
Energy Balance	
Overall	$((PURMAP)F_{52}^{(MAP)}/M^{(MAP)}H_{52}^{(MAP)}+(PURDAP)F_{57}^{(DAP)}/M^{(DAP)}H_{57}^{(DAP)}+$ $F_{76}^{(H_2O)}/M^{(H_2O)}H_{76}^{(H_2O)})-(\Sigma F_{40}^{(i)}/M^{(i)}H_{40}^{(i)}+F_{42}^{(NH_3)}/M^{(NH_3)}H_{42}^{(NH_3)})$ $+Q_{out}(F_{52}+F_{57})-Q_{APG}=0$ $i = P_2O_5, H_2O$
Enthalpy Function	$H_k^i(T)=(a_1^i+\frac{1}{2}a_2^iT+\frac{1}{3}a_3^iT^2+\frac{1}{4}a_4^iT^3+\frac{1}{5}a_5^iT^4+\frac{b_1^i}{T})RT$ J/mol $i = H_2O, NH_3$ $k = 40, 42, 76$ $H^{(P_2O_5)}=(-1278.437)(1000)+106.014(T-298.15)J/mol$ Source: Lide (1982) $H_k^{(MAP)}=((-345.38)(1000)+34.00(T-298.15))4.182$ J/mol k=52 Source: Lide (1982) $H_k^{(DAP)}=((-374.50)(1000)+45.00(T-298.15))4.182$ J/mol k=57 Source: Lide (1982)

List, 1998).

- CF Industries, Donaldsonville (770 thousand metric tons per year)

- PCS Nitrogen Fertilizer LP, Geismar (1.1 million metric tons per year)

For UAN production, the capacity of 183 tons per day was used in the base case (Hertwig, 2004).

B-10-1. Process Description

UAN is simply manufactured by mixing granular urea and ammonium nitrate solution. The block diagram is shown in Figure 4.11 with the stream definitions in Table 4-30.

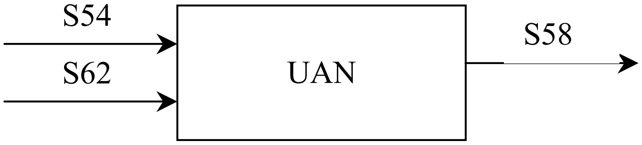


Figure 4.11 Block Diagram of UAN Plant

Table 4-30 Description of Process Streams in UAN Plant

Name of Streams	Description
Input Streams	
S54	Granular urea to UAN plant
S62	Ammonium nitrate solution to UAN plant
Output Streams	
S58	UAN solution produced from UAN plant

B-10-2. Material Balance and Energy Balance

Using the parameters in Table 4-31 the material balance and energy balance of UAN plant are given in Table 4-32. In Table 4-32, the overall material balance for the whole process is given with the mixture stream expressions. For the species material balance, the first equation is for the N balance; the second one is for the water balance.

An energy balance is not required because there is no significant energy change in this simple blending process. Hence, for the material and energy balance, there are 7 variables and 6 equations, so the number of degrees of freedom is 1.

Table 4-31 Parameters in UAN Production, from Hertwig (2004)

Name	Meaning	Value
CONCAMN	$AmNO_3$ solution strength, $AmNO_3$ weight fraction	0.30
CONCNUAN	UAN solution N weight fraction (commercial spec 0.28-0.32)	0.30

Table 4-32 Constraint Equations for UAN Production

Material Balance	
Overall	$(F_{54} + F_{62}) - F_{58} = 0$ where $F_{58} = F_{58}^{(UAN)} + F_{58}^{(H_2O)}$ $F_{62} = F_{62}^{(AN)} + F_{62}^{(H_2O)}$
Species	N: $(\frac{28.02}{60.07}F_{54} + \frac{28.02}{80.06}F_{62}^{(AN)}) - (CONCNUAN)F_{58} = 0$ H_2O: $F_{62}^{(H_2O)} - F_{58}^{(H_2O)} = 0$

B-11. Power Generation (Hertwig, 2004)

In the chemical production complex in the lower Mississippi River corridor, the power generation plants are in the IMC-Argico Uncle Sam and Faustina plants (Hertwig, 2004).

B-11-1. Process Description

A steam turbine-driven generator is used in the complex. This is driven by steam produced from waste process heat. The steam turbine-driven power generation plant uses waste-heat steam from the sulfuric acid plant, and there are two generators; one is for high pressure steam (HP) and the other is for intermediate pressure steam

(IP). Also there is a package boiler in the plant to provide needed steam not otherwise available. The block diagram is shown in Figure 4.12 with the stream definitions in Table 4-33.

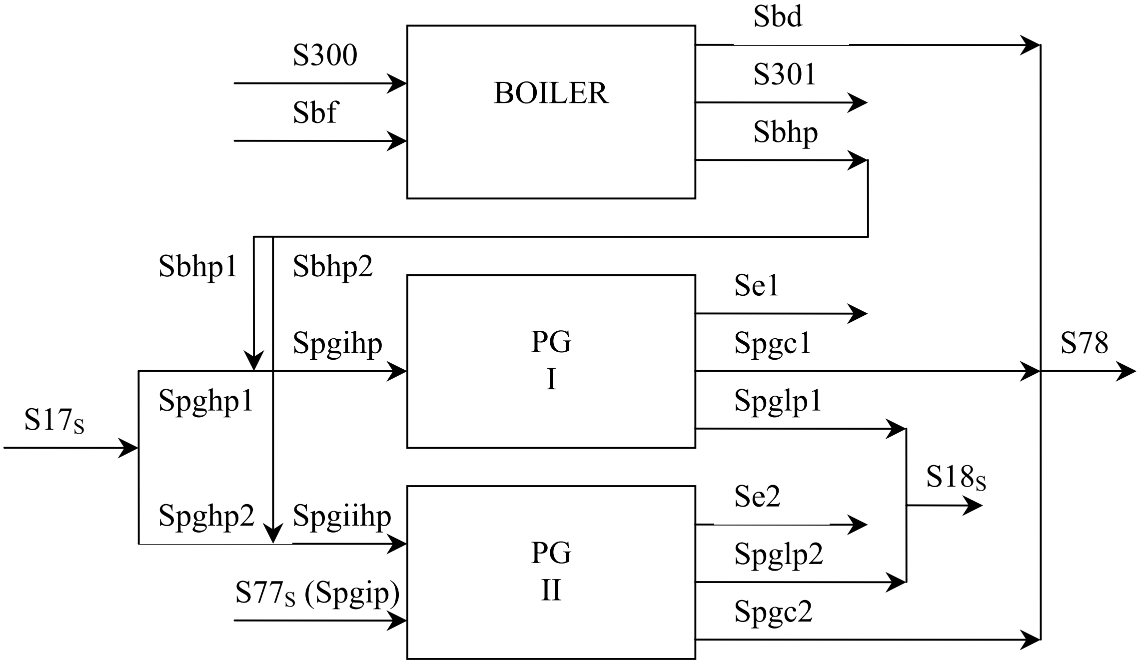


Figure 4.12 Block Diagram of Power Generation Plant

B-11-2. Material Balance and Energy Balance

Using the parameters in Table 4-34 the material balance and energy balance of power generation plant are given in Table 4-35. In Table 4-35, the overall water balance for the whole process is given with the expressions of mixing and splitting streams. For the species (water) material balance, the first equation is for the low pressure steam (LP) balance in power generator I (PGI); the second one is for the condensed water balance in PGI; the third one is for the LP balance in power generator II (PGII); the fourth one is for the condensed water balance in PGII; the fifth one is for the intermediate pressure steam (IP) balance in PGII; the sixth one is for the boiler feed water (BFW) balance in the package boiler; the seventh one is for the high pressure steam (HP) balance in the package boiler; the last one is for the distribution of HP from the package boiler to PGII. Meanwhile, the material balances of methane and CO_2 are also shown in Table 4-35 which gives the energy source and CO_2 emissions.

Table 4-33 Description of Process Streams in Power Generation Process

Name of Streams	Description
Input Streams	
$S17_S$	HP steam from sulfuric acid plant
$S77_S$	IP steam from sulfuric acid plant
Sbf	Water to the package boiler
S300	Natural gas to the package boiler
Intermediate Streams	
Spghp1	One branch of $S17_S$ to power generator I (PGI)
Spghp2	The other branch of $S17_S$ to power generator II (PGII)
Spglp1	LP from PGI
Spglp2	LP from PGII
Spgip	Branch of $S77_S$
Sbd	Blow-down water from the package boiler
Spgc1	Condensate water from PGI
Spgc2	Condensate water from PGII
Spgihp	HP to PGI
Spgiihp	HP to PGII
Sbhp	HP produced from the package boiler
Sbhp1	One branch of HP produced from the package boiler
Sbhp2	The other branch of HP produced from the package boiler
Output Streams	
S78	Water from power generation plant
$S18_S$	LP steam from power generation plant
S301	CO_2 emission from the boiler
Se1	electricity generated from turbo generator
Se2	electricity generated from IP turbo generator

In the overall energy balance, Q_{PG} is heat output of the power plant in the form of steam, and electricity. Part of the steam produced from power plant is used in the

Table 4-34 Parameters in Power Generation, from Hertwig (2004)

Name	Meaning	Value
HPPLP	Conversion coefficient from HP to LP (KPPH HP per KPPH LP produced)	1.05
IPPLP	Conversion coefficient from IP to LP (KPPH IP per KPPH LP produced)	24.15
BDPG	Blowdown based on HP product	0.08
ENNATB	CH_4 combustion heat (MJ per cubic meter)	37.56
ROUNATB	CH_4 gas density (g per cubic meter)	653.921
HPNATB	Klb HP produced per MBTU CH_4 fired	0.9

Table 4-35 Constraint Equations for Power Generation Process

Material Balance	
Overall	$(F_{S17} + F_{S77} + F_{bf}) - (F_{S18} + F_{S78}) = 0$ (water balance) where $F_{S17} = F_{pghp1} + F_{pghp2}$ $F_{S77} = F_{pgip}$ $F_{S18} = F_{pglp1} + F_{pglp2}$ $F_{S78} = F_{bd} + F_{pgc1} + F_{pgc2}$ $F_{bhp} = F_{bhp1} + F_{bhp2}$ $F_{pgihp} = F_{pghp1} + F_{bhp1}$ $F_{pgiihp} = F_{bhp2} + F_{pghp2}$
Species (Water)	LP in PGI: $F_{pgihp} - (HPPLP)F_{pglp1} = 0$ Condensed water in PGI: $F_{pgc1} - (F_{pgihp} - F_{pglp1}) = 0$ LP in PGII: $(\frac{1}{HPPLP}F_{pgiihp} + \frac{1}{IPPLP}F_{pgip}) - F_{pglp2} = 0$ Condensed water in PGII: $F_{pgc2} - (F_{pgiihp} + F_{pgip} - F_{pglp2}) = 0$ IP in PGII: $F_{pgip} - 1.15F_{pgiihp} = 0$ BFW in boiler: $F_{bf} - (F_{bd} + F_{bhp}) = 0$ HP in boiler: $F_{bd} - (BDPG)F_{bhp} = 0$ HP from boiler to PGII: $F_{bhp2} = 0$
Species (CH_4, CO_2)	CH_4: $F_{300} - \frac{(2204.62)(1.055)(ROUNATB)}{(HPNATB)(ENNATB)}F_{bhp} = 0$

Table 4-35 Continued

Material Balance (Continued)	
Species (CH_4, CO_2)	CO_2: $\frac{F_{300}}{16.05}-\frac{F_{301}}{44.01}=0$
Energy Balance	
Overall	$Q_{PG}-(-(Se_1+Se_2)+(\frac{-285830}{18.02}-H_{lpp})F_{18})=0$ where $S_{e1}=$ $\frac{(365.25)(24)(3600)}{(9.6)}(\frac{2204.62}{(365.25)(24)(1000)}F_{pgihp}-15E-05$ $-\frac{2204.62}{(365.25)(24)(1000)(1.8)}F_{pglpl})$ 1E+11 J/year, from Hertwig (2004) $S_{e2}=\frac{(365.25)(24)(3600)}{(9.6)}(\frac{2204.62}{(365.25)(24)(1000)}F_{pgiihp}$ $+\frac{2204.62}{(365.25)(24)(1000)(1.4)}F_{pgip}-15E-05-\frac{2204.62}{(365.25)(24)(1000)(1.8)}F_{pglp2})$ 1E+11 J/year, from Hertwig (2004)
Enthalpy Function	$H^{(LP)}(T)=((72.558+(0.5)(-0.66244)T+(\frac{1}{3})(0.002562)T^2+$ $(0.25)(-4.3659E-06)T^3+(0.2)(2.7818E-09)T^4+\frac{(-41886)}{T})(8.3145)T$ $-1893)\frac{1}{18.02}+((-0.007)T^2+(2.7838)T+2292.0563)$ J/g, LP has no super heat, from Meyer, et al. (1977) and McBride, et al. (1993).

phosphoric acid plant. The other part of the steam is used in other plants which require heat input in the base case. Electricity from the power plant is considered to be interchangable with steam since both steam and electricity can be used to drive pumps, compressors and other prime movers. The electrity Se1 and Se2 are calculated by the formulas in Table 4-35 provided by Hertwig (2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, only complete water balance is given in Table 4-35, where there are 22 variables and 19 equations, so the number of degrees of freedom is 3. For the material and energy balance of water, there are 40 variables and 30 equations, so the number of degrees of freedom is 10.

B-12. Conventional Acetic Acid Production (Rudd, et al., 1981; Louisiana Chemical and Petroleum Products List, 1998)

In the chemical production complex in the lower Mississippi River corridor, acetic acid is produced by the following plants (Louisiana Chemical & Petroleum Products List, 1998).

- Borden Chemicals and Plastics, Geismar (Not available)
- Dow Chemical, Hahnville (18 million pounds per year)

For acetic acid production, the production rate of the Dow Chemial's Hahnville plant, 18 million pounds per year (8,160 metric tons per year), was used in the base case (Louisiana Chemical & Petroleum Products List, 1998).

B-12-1. Process Description

A Monsanto developed low-pressure process to produce acetic acid from methanol and CO is used in Dow Chemical's Hahnville plant. The selectivity based on methanol was over 99%. CO was produced from methane and CO_2 (Equation 4-21 and 4-32). The specific reaction for producing acetic acid was Equation (4-41). The overall reaction was Equation (4-42) obtained from Equation (4-21), (4-32) and (4-41). The block diagram is illustrated in Figure 4.13 with the stream definitions from Table 4-36.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{4-21}$$

$$CO_2 + H_2 \rightarrow CO + H_2O \tag{4-32}$$

$$CH_3OH + CO \rightarrow CH_3COOH \tag{4-41}$$

$$CH_4 + 3CO_2 + 4CH_3OH \rightarrow 4CH_3COOH + 2H_2O \tag{4-42}$$

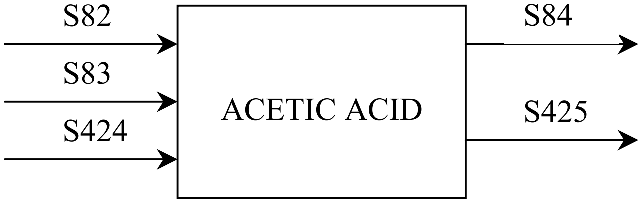


Figure 4.13 Block Diagram of Conventional Acetic Acid Plant

Table 4-36 Description of Process Streams in Conventional Acetic Acid Plant

Name of Streams	Description
Input Streams	
S82	CO_2 to conventional acetic acid plant
S83	Natural gas to conventional acetic acid plant
S424	Methanol from methanol plant to conventional acetic acid plant
Output Streams	
S84	Production of acetic acid from conventional acetic acid plant
S425	Water produced from conventional acetic acid plant

B-12-2. Material Balance and Energy Balance

Using the parameters in Table 4-37, the material balance and energy balance of conventional acetic acid plant are given in Table 4-38.

In Table 4-38, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equations (4-21, 4-32, 4-41 and 4-42), the first equation is for the CO_2 balance; the second one is for the CH_4 balance; the third one is for the methanol balance; the last one is for the H_2O balance.

Table 4-37 Parameters in Conventional Acetic Acid Plant

Name	Meaning	Value
	CO_2 utilization	1.0
	CH_4 utilization	1.0
	Methanol utilization	1.0

Table 4-38 Constraint Equations for Conventional Acetic Acid Plant

Material Balance

Overall $F_{82}+F_{83}+F_{424}-F_{84}-F_{425}=0$

Species

CO_2: $\frac{1}{(44.01)(3)}F_{82}-\frac{1}{(60.06)(4)}F_{84}=0$

CH_4: $\frac{1}{16.05}F_{83}-\frac{1}{(60.06)(4)}F_{84}=0$

Methanol: $\frac{1}{(32.05)(4)}F_{424}-\frac{1}{(60.06)(4)}F_{84}=0$

H_2O: $-F_{425}+\frac{(2)(18.02)}{(60.06)(4)}F_{84}=0$

Energy Balance

Overall $(F_{84}^{(aceticacid)}/M^{(aceticacid)}H_{84}^{(aceticacid)}+F_{425}^{(H_2O)}/M^{(H_2O)}H^{(H_2O)})-(F_{82}^{(CO_2)}$

$/M^{(CO_2)}H_{82}^{(CO_2)}+F_{83}^{(CH_4)}/M^{(CH_4)}H_{83}^{(CH_4)}+F_{424}^{(CH_3OH)}/M^{(CH_3OH)}H_{424}^{(CH_3OH)})$

$+Q_{out}F_{84}^{(aceticacid)}-Q_{AA}=0$

Enthalpy Function $H_k^i(T)=(a_1^i+\frac{1}{2}a_2^iT+\frac{1}{3}a_3^iT^2+\frac{1}{4}a_4^iT^3+\frac{1}{5}a_5^iT^4+\frac{b_1^i}{T})RT$ J/mol

i = CO_2, CH_4, H_2O; k = 82, 83, 425

$H_k^{(MeOH)}(T)=(-238.54)(1000)+(79.225)(T-298.15)$ J/mol k=424

Source: Felder and Roussleu (1986).

$H_k^{(aceticacid)}(T)=((-115.8)(1000)+(29.7)(T-298.15))(4.185)$ J/mol k=425

Source: Lide (1982).

In the overall energy balance, Q_{AA} is heat input of the acetic acid plant in the form of steam in the heat exchanger and acetic acid separation units, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in the heat exchanger and condensers in acetic acid plant based on the unit of acetic acid product, 15 MJ per lb of acetic acid (Rudd, et al., 1981). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 5 variables and 5 equations including the dependent overall mass balance, so the number of degrees of freedom is 1. For the material and energy balance, there are 16 variables and 11 equations including the dependent overall mass balance, so the number of degrees of freedom is 6.

B-13. Ethylbenzene (EB) Produced from Benzene and Ethylene (Louisiana Chemical & Petrochemical Products List, 1998; Pellegrino, 2000; Speight, 2002; Brown, et al., 1985)

In the lower Mississippi River corridor, ethylbenzene is produced by the plants as follow (Louisiana Chemical & Petroleum Products List, 1998).

- Chevron Chemical Company, St. James (1.9 billion pounds per year)
- Cos-mar Company, Carville (2.2 billion pounds per year)
- Deltech Corporation, Baton Rouge (700 million pounds per year)

For ethylbenzne production, the production rate of ethylbenzene in St. James plant of Chevron Chemical Company, 1.9 billion pounds per year (862,000 metric tons per year), was used in the base case (Louisiana Chemical & Petrochemical Products List, 1998).

B-13-1. Process Description

Since 1980, EB has been produced using zeolite catalysts in a liquid phase operation (Equation 4-43) (Pellegrino, 2000). Ethylene and benzene are fed into a liquid-filled alkylation reactor that contains fixed beds of zeolite catalyst. The reaction needs excess benzene, in ratios of about 1:0.6 benzene to ethylene. The recyclable alkylbenzenes and other by-products can be recycled to produce additional EB. A product with purity as high as 99.95 to 99.99% can be achieved. Since nearly all the EB produced (99%) is used to produce styrene, this process is usually integrated with styrene production, which is very energy-intensive. The block diagram of direct oxidation of ethylene process is in Figure 4.14 with the stream description in Table 4-39.

$$C_6H_6 + CH_2 = CH_2 \rightarrow C_6H_5CH_2CH_3 \qquad (4\text{-}43)$$

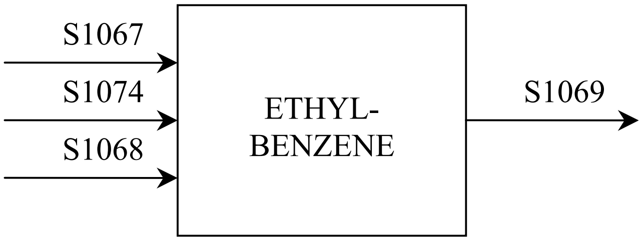


Figure 4.14 Block Diagram of Ethylbenzene Process

Speight (2002) reported that the overall yield of EB is 98% with the elaborate separations required, including washing with caustic and water and three distillation column, i.e. benzene column (benzene recycle), EB column and polyethylbenzene column (to transalkylator).

Table 4-39 Description of the Streams in the Ethylbenzene Process

Stream Name	Stream Description
Input Streams	
S1067	Benzene to Ethylbenzene process
S1068	Ethylene to Ethylbenzene process
S1074	Benzene recycled from Styrene process
Output Streams	
S1069	EB produced from Ethylbenzene process

B-13-2. Material Balance and Energy Balance

Using the parameters in Table 4-40, the material balance and energy balance of ethylbenzene process are given in Table 4-41.

In Table 4-41, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equation (4-43), the first equation is for the C_2H_4 balance; and the second one is for the benzene balance.

Table 4-40 Parameters in EB Production

Name	Meaning	Value
	Ethylene benzene yield in EG plant	100%
	Ethylene and benzene conversions	100%

Table 4-41 Constraint Equations for EB Production

Material Balance	
Overall	$(F_{1067}+F_{1074}+F_{1068})-F_{1069}=0$
Species	C_2H_4: $\frac{-F_{1068}}{mw(C_2H_4)}+\frac{F_{1069}}{mw(EB)}=0$
	Benzene: $-\frac{(F_{1067}+F_{1074})}{mw(benzene)}+\frac{F_{1069}}{mw(EB)}=0$
Energy Balance	
Overall	$F_{1069}^{(EB)}/M^{(EB)}H_{1069}^{(EB)}-(F_{1067}^{(BENZENE)}/M^{(BENZENE)}H_{1067}^{(BENZENE)}$ $+F_{1074}^{(BENZENE)}/M^{(BENZENE)}H_{1074}^{(BENZENE)}+F_{1068}^{(C_2H_4)}/M^{(C_2H_4)}H_{1068}^{(C_2H_4)})$ $+Q_{out}F_{1069}^{(EB)}-Q_{EB}=0$
Enthalpy Function	$H_k^i(T)=(a_1^i+\frac{1}{2}a_2^iT+\frac{1}{3}a_3^iT^2+\frac{1}{4}a_4^iT^3+\frac{1}{5}a_5^iT^4+\frac{b_1^i}{T})RT$ J/mol i = BENZENE, C_2H_4 k = 1067, 1068, 1074 $H_{1069}^{(EB)}=-12300+185.572(T-298.15)$ J/mol Source: Lide (1990) and NIST (National Institute of Standards and Technology) (2002)

In the overall energy balance, Q_{EB} is heat input of the ethylbenzene process in the form of steam in the heat exchanger and separation distillation column reboilers, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in the heat exchanger and separation distillation column condensers in the ethlbenzene process based on the unit of ethylbenzene product, 96 KJ per lb of ethylbenzene (Brown, et al., 1985). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 4 variables and 3 equations including one dependent one (overall material balance), so the number of degrees of freedom is 2. For the material and energy balance, there are 13 variables and 8 equations including one dependent one (overall material balance), so the number of degrees of freedom is 6.

B-14. Styrene from Catalytic Dehydrogenation of Ethylbenzene (Conventional Styrene Process) (Louisiana Chemical & Petrochemical Products List, 1998; Pellegrino, 2000; Wells, 1999; Brown, et al., 1985)

In the lower Mississippi River corridor, styrene is produced by the plants as follow (Louisiana Chemical & Petroleum Products List, 1998).

- Chevron Chemical Company, St. James (1.7 billion pounds per year)
- Cos-mar Company, Carville (2 billion pounds per year)
- Deltech Corporation, Baton Rouge (800 million pounds per year)

For styrene production, the production rate of Chevron Chemical Company in St. James plant, 1.7 billion pounds per year (771,000 metric tons per year), was used in the base case (Louisiana Chemical & Petroleum Products List, 1998).

B-14-1. Process Description

Styrene is widely used in copolymers as well as in homopolymers and rubber-modified styrene polymers. The major process for styrene manufacture involves a Friedel-Crafts reaction between benzene and ethylene to form EB. Styrene and hydrogen can be produced from dehydrogenation to styrene in the presence of steam and a catalyst (Equation 4-44).

Most of the styrene produced in the US is made by dehydrogenation of EB (Equation 4-44) (Pellegrino, 2000). The by-products are minor amounts of tar, toluene, and benzene (Equation 4-45, 4-46 and 4-47). Benzene, toluene and unreacted EB are recycled; tar residues are used as fuel. Conversion of EB can be as high as 80-90%. The catalysts are various metal oxides, such as zinc, iron, or magnesium oxides coated on activated carbon, alumina, or bauxite. The reaction temperature is 649 °C and under vacuum. The yield of styrene is 90% (Wells, 1999).

The block diagram of conventional styrene process is in Figure 4.15 with the stream description in Table 4-42.

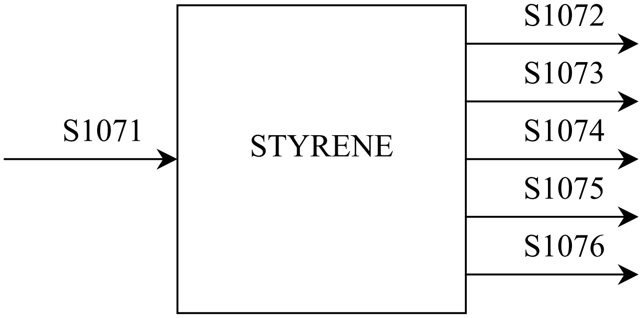
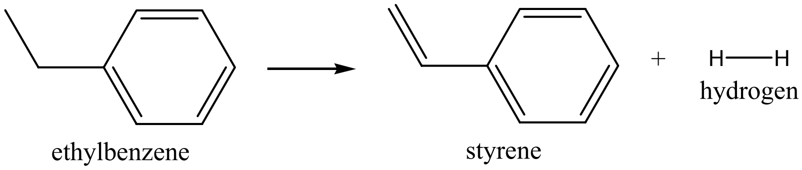
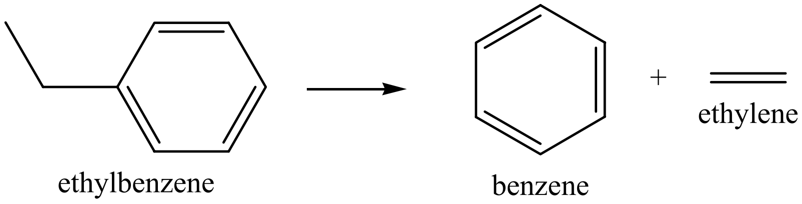


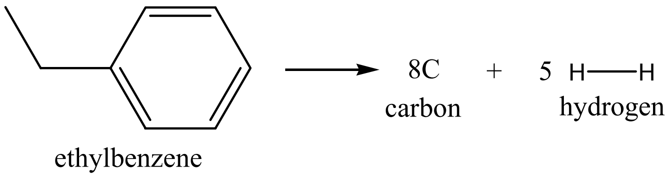
Figure 4.15 Block Diagram of Conventional Styrene Process



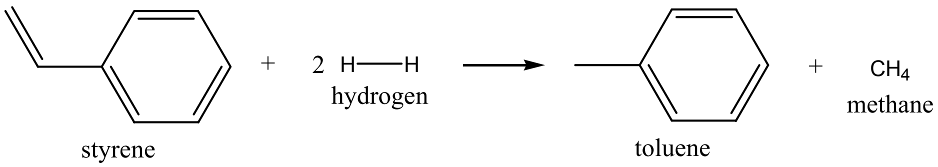
(4-44)



(4-45)



(4-46)



(4-47)

Table 4-42 Description of the Streams in Conventional Styrene Process

Stream Name	Stream Description
Input Streams	
S1071	Ethylbenzene to conventional styrene plant
Output Streams	
S1072	Styrene produced from conventional styrene plant
S1073	Fuel gas produced from conventional styrene plant
S1074	Benzene produced from conventional styrene plant
S1075	Toluene produced from conventional styrene plant
S1076	Carbon produced from conventional styrene plant

B-14-2. Material Balance and Energy Balance

Using the parameters in Table 4-43, the material and energy balances of conventional styrene process are given in Table 4-44.

In Table 4-44, the overall material balance for the whole process is given with the mixture stream expression. For the species material balance obtained using the reaction equations (4-44, 4-45, 4-46 and 4-47), the first equation is for the styrene balance; and the second one is for the benzene balance; the third one is for the toluene balance; the fourth one is for the carbon balance; the fifth one is for the H_2 balance; the sixth one is for the C_2H_4 balance; the last one is for the CH_4 balance.

In the overall energy balance, Q_{STY} is heat input of the conventional styrene process in the form of steam to supply enough heat for the endothermic reaction and for the product separation, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in heat exchanger and condensers in the conventional styrene process based on the unit of styrene product, 1.4 MJ per lb of styrene (Brown, et al., 1985). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 9 variables and 9 equations including one dependent one (overall material balance), so the number of degrees of freedom is 1. For the material and energy balances, there are 24 variables and 18 equations including one dependent one (overall material balance), so the number of degrees of freedom is 7.

Table 4-43 Parameters in Conventional Styrene Process

Name	Meaning	Value
SSTS	Selectivity of EB to styrene in conventional styrene process	0.90
SSTB	Selectivity of EB to benzene in conventional styrene process	0.08
SSTC	Selectivity of EB to carbon in conventional styrene process	0.02
SSCTT	Conversion of styrene to toluene in conventional styrene process	0.01
	Conversion of EB in conventional styrene process	100%

Table 4-44 Constraint Equations for Conventional Styrene Process

Material Balance	
Overall	$F_{1071}-(F_{1072}+F_{1073}+F_{1074}+F_{1075}+F_{1076})=0$ where $F_{1073}=F_{1073}^{(H_2)}+F_{1073}^{(C_2H_4)}+F_{1073}^{(CH_4)}$
Species	Styrene: $\frac{F_{1072}}{mw(styrene)}-\frac{F_{1071}\times SSTS\times(1-SSCTT)}{mw(EB)}=0$ Benzene: $\frac{F_{1074}}{mw(benzene)}-F_{1071}\frac{SSTB}{mw(EB)}=0$ Toluene: $\frac{F_{1075}}{mw(toluene)}-F_{1071}\frac{SSTS\times SSCTT}{mw(EB)}=0$ C: $\frac{F_{1076}}{mw(C)}-\frac{F_{1071}\times SSTC}{mw(EB)}\times 8=0$ H$_2$: $\frac{F_{1073}^{(H_2)}}{mw(H_2)}-(F_{1071}\frac{SSTS}{mw(EB)}+F_{1071}\frac{SSTC\times 5}{mw(EB)}-\frac{2F_{1075}}{mw(toluene)})=0$ C$_2$H$_4$: $\frac{F_{1073}^{(C_2H_4)}}{mw(C_2H_4)}-\frac{F_{1074}}{mw(benzene)}=0$ CH$_4$: $\frac{F_{1073}^{(CH_4)}}{mw(CH_4)}-\frac{F_{1075}}{mw(toluene)}=0$
Energy Balance	
Overall	$(F_{1072}^{(STYRENE)}/M^{(STYRENE)}H_{1072}^{(STYRENE)}+\sum F_{1073}^{(i)}/M^{(i)}H_{1073}^{(i)}$ $+F_{1074}^{(BENZENE)}/M^{(BENZENE)}H_{1074}^{(BENZENE)}+F_{1075}^{(TOLUENE)}/M^{(TOLUENE)}H_{1075}^{(TOLUENE)}$ $+F_{1076}^{(C)}/M^{(C)}H_{1076}^{(C)})-F_{1071}^{(EB)}/M^{(EB)}H_{1071}^{(EB)}+Q_{out}F_{1072}^{(STYRENE)}-Q_{STY}=0$ i = H$_2$, CH$_4$, C$_2$H$_4$
Enthalpy Function	$H_k^i(T)=(a_1^i+\frac{1}{2}a_2^iT+\frac{1}{3}a_3^iT^2+\frac{1}{4}a_4^iT^3+\frac{1}{5}a_5^iT^4+\frac{b_1^i}{T})RT$ J/mol i = H$_2$, CH$_4$, C$_2$H$_4$, BENZENE, C k = 1073, 1074, 1076 $H_{1071}^{(EB)}=-12300+185.572(T-298.15)$ J/mol Source: Lide (1990) and NIST (2002) $H_{1072}^{(STYRENE)}=103400+183.2(T-298.15)$ J/mol Source: NIST (2002) $H_{1075}^{(TOLUENE)}=12000+157.09(T-298.15)$ J/mol Source: NIST (2002)

B-15. Relations of Chemical Plants in the Base Case

The streams not defined in the above plant models are described in Table 4-45. The stream splits and mixing points for mass balance in the base case of chemical production complex are given in Table 4-46, and for temperatures and pressures in the energy balance are given in Table 4-47.

Table 4-45 Description of Process Streams in the Base Case

Name of Streams	Description
S5	Total air input to the base case
S6	Total natural gas input to the base case
Sapply	Steam available for the base case
S30	NH_3 from NH_3 plant to ammonium nitrate plant and for sale
S43	NH_3 for sale
SCDEM	Total impure CO_2 emissions from the base case
S59	Urea for sale
S423	Methanol for sale

Table 4-46 Stream Splits and Mixing Points for Mass Balance in the Base Case

Relationship	Description
$F_2 + F_3 = F_4$	Sulfur from Frasch mines/wells and Claus recovery to sulfuric acid plant
$F_5 = F_7 + F_8 + F_9$	Air to sulfuric acid, nitric acid and ammonia plant
$F_6 = F_{10} + F_{11} + F_{300} + F_{83}$	Natural gas to ammonia, methanol, power plant and acetic acid plant
$F_{16} + F_{18}$ $= F_{24} + F_{27} + F_{28} + F_{apply}$	LP steam from sulfuric acid and power plant to phosphoric acid, urea and other plants as heat input
$F_{19} = F_{29} + F_{30} + F_{31} + F_{42}$	Ammonia from ammonia plant to nitric acid, ammonium nitrate, ammonium phosphate, urea plant and for sale
$F_{20} = F_{32} + F_{33} + F_{64} + F_{82}$	CO_2 from ammonia plant to urea, methanol, acetic acid plant and emission to atmosphere
$F_{30} = F_{43} + F_{44}$	Ammonia to ammonium phosphate plant and for sale
$F_{46} = F_{54} + F_{59}$	Urea from urea plant to UAN plant and for sale
$F_{60} = F_{39} + F_{40} + F_{41}$	Phosphoric acid from phosphoric acid plant to GTSP, ammonium phosphate plant and for sale
$F_{47} = F_{423} + F_{424}$	Methanol from methanol plant to acetic acid plant and for sale

Table 4-46 Continued

Relationship	Description
$F_{1069} = F_{1070} + F_{1071}$	Ethylbenzene from ethylbenzene plant to styrene plant and for sale
$F_{CDEM} = F_{301} + F_{801}$ $+ F_{81}^{(CO_2)} + F_{15}^{(CO_2)} + F_{802}^{(CO_2)}$	Impure CO_2 emissions from power plant, urea, nitric acid, sulfuric acid and methanol plants

Table 4-47 Stream Temperatures and Pressures for Energy Balance in the Base Case

Relationship	Description
Tlp = Ts24	LP from sulfuric acid plant ($S16_S$) and LP to phosphoric acid plant ($S24_S$) have same temperature.
Tlp = Tlpp	LP from sulfuric acid plant ($S16_S$) and LP from power plant ($S18_S$) have same temperature.
TO2b = TO2a	Air to nitric acid plant (S8) and air to ammonia plant (S9) have same temperature.
TNH3a = TNH3b	NH_3 from NH_3 plant (S19) and NH_3 to nitric acid plant (S29) have same temperature.
TNH3a = TNH3i	NH_3 from NH_3 plant (S19) and NH_3 to urea plant (S31) have same temperature.
TNH3a = TNH3k	NH_3 from NH_3 plant (S19) and NH_3 to MAP and DAP plant (S42) have same temperature.
TNH3a = TNH3j	NH_3 from NH_3 plant (S19) and NH_3 to ammonium nitrate plant (S29) have same temperature.
TCO2c = TCO2i	CO_2 from NH_3 plant (S20) and CO_2 to urea plant (S32) have same temperature.
TCO2c = TCO2h	CO_2 from NH_3 plant (S20) and CO_2 to methanol plant (S33) have same temperature.
Taq = Ta	Nitric acid from nitric acid plant (S45) and nitric acid to ammonium nitrate plant (S45) have same temperature.
TCH4a = TCH4h	CH_4 to NH_3 plant (S10) and CH_4 to methanol plant (S11) have same temperature.
Thp39 = Thp40	Phosphoric acid to GTSP plant (S39) and phosphoric acid to MAP and DAP plant (S40) have same temperature.
TCO2c = Ts82	CO_2 from NH_3 plant (S20) and CO_2 to acetic acid plant (S82) have same temperature.
TCH4a = Ts83	CH_4 to NH_3 plant (S10) and CH_4 to acetic acid plant (S83) have same temperature.
Tmet = Ts424	Methanol from methanol plant (S47) and methanol to acetic acid plant (S424) have same temperature.
T('1069') = T('1071')	Ethylbenzene from ethylbenzene plant (S1069) and ethylbenzene to styrene plant (S1071) have same temperature.

C. New Processes Added in Chemical Production Complex - Superstructure

New chemical processes are incorporated into the chemical production complex (base case) in the lower Mississippi River corridor. This gives a superstructure of existing and new plants in the chemical production complex. This superstructure is used to select the optimum configuration of existing and new plants that maximize the triple bottom line. These new processes include ones using carbon dioxide that is now being vented to the atmosphere and alternate processes that have advantages over existing ones.

C-1. Electric Furnace Phosphoric Acid (Austin, 1984)

The capacity of this process is set as the same as the wet process for phosphoric acid production, 3833 TPD. This process can produce food grade phosphoric acid, and the wastes are $CaSiO_3$ and CO_2.

C-1-1. Process Description

This method uses phosphate rock, sand and coke to produce phosphoric acid as shown in the block diagram in Figure 4.16 with the description of streams shown in Table 4-48. This process produces high purity phosphoric acid which is used in food grade applications. The reaction can be expressed as:

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 9SiO_2 + 15C = CaF_2 + 6P + 15CO + 9CaSiO_3 \qquad (4\text{-}48)$$

$$4P + 5O_2 = 2P_2O_5 \qquad (4\text{-}49)$$

$$P_2O_5 + 3H_2O = 2H_3PO_4 \qquad (4\text{-}50)$$

or, more simply expressed,

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C + 5O_2 + 3H_2O = 3CaSiO_3 + 2H_3PO_4 + 5CO_2 \quad (4\text{-}51)$$

The phosphate rock was first ground and sized and mixed with sand and coke. Then the mixture is sintered and introduced into the electric furnace. After the mixture is heated and reduced at an elevated temperature, phosphorous vapor is condensed, and CO is drawn off. Then in a separate step the phosphorus is burned in air and hydrated to become phosphoric acid solution.

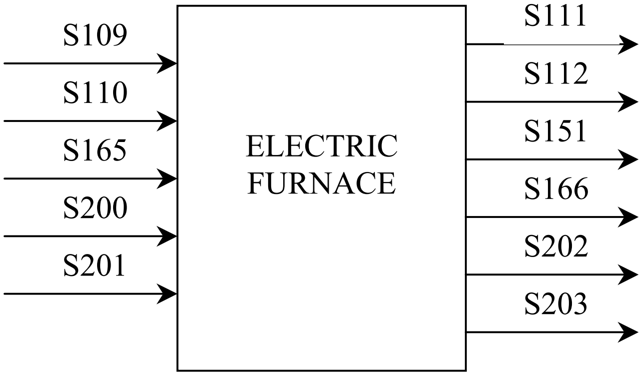


Figure 4.16 Block Diagram of Electric Furnace Process

Table 4-48 Description of Electric Furnace Process (EFP) Streams

Name of Streams	Description
Input Streams	
S109	Ore to EFP
S110	Sand to EFP
S165	C needed in EFP
S200	Air needed for EFP
S201	H_2O needed for EFP
Output Streams	
S111	Production of $CaSiO_3$ from EFP
S112	Production of H_3PO_4 from EFP
S151	Vent gas from EFP
S166	CO_2 produced from C in EFP
S202	CaF_2 produced from EFP
S203	Inert impurity in the ore separated in EFP

C-1-2. Material Balance and Energy Balance

The parameters in the electronic furnace process are shown in Table 4-49 and the constraint equations for the material and energy balances are given in Table 4-50.

Table 4-49 Parameters in Electric Furnace Process, from Austin (1984)

Name	Meaning	Value
CONCPEF	P_2O_5 concentration produced from EFP	0.6156
CONCPOR	P_2O_5 concentration in the rock (weight fraction)	0.365

Table 4-50 Constraint Equations for Electric Furnace Process

Material Balance	
Overall	$(F_{109} + F_{110} + F_{165} + F_{200} + F_{201}) - (F_{112} + F_{111} + F_{166} + F_{151} + F_{202} + F_{203}) = 0$
	where $F_{112} = F_{112}^{(P_2O_5)} + F_{112}^{(H_2 0)}$
	$F_{151} = F_{151}^{(N_2)} + F_{151}^{(CO_2)} + F_{151}^{(Ar)}$
	$F_{200} = F_{200}^{(O_2)} + F_{200}^{(N_2)} + F_{200}^{(CO_2)} + F_{200}^{(Ar)}$
Species	P_2O_5 : $(CONCPOR)F_{109} - F_{112}^{(P_2O_5)} = 0$
	CO_2 : $\frac{44.01}{12.01}F_{165} - F_{166} = 0$
	SiO_2 : $\frac{CONCPOR}{141.94}F_{109} - \frac{1}{(60.09)(3)}F_{110} = 0$
	C : $\frac{CONCPOR}{141.94}F_{109} - \frac{1}{(5)(12.01)}F_{165} = 0$
	$CaSiO_3$: $\frac{1}{(60.09)(3)}F_{110} - \frac{1}{(3)(116.17)}F_{111} = 0$
	O_2 : $\frac{CONCPOR}{141.94}F_{109} - \frac{1}{(5)(32)}F_{200}^{(O_2)} = 0$
	N_2 : $F_{200}^{(N_2)} - F_{151}^{N_2} = 0$
	Ar : $F_{200}^{(Ar)} - F_{151}^{Ar} = 0$
	Vent CO_2 : $F_{200}^{(CO_2)} - F_{151}^{CO_2} = 0$
	H_2O : $F_{201} - F_{112}^{(H_2O)} = 0$
	CaF_2 : $\frac{(CONCPOR)(78.08)}{(3)(141.94)}F_{109} - F_{202} = 0$
	Impurity : $(1 - \frac{(CONCPOR)(310.18)}{141.94}(1 + \frac{78.08}{(3)(310.18)}))F_{109} - F_{203} = 0$

Table 4-50 Continued

Energy Balance	
Overall	$(\Sigma F_{112}^{(i)}/M^{(i)}H_{112}^{(i)} + \Sigma F_{151}^{(j)}/M^{(j)}H_{151}^{(j)} + F_{166}/M^{(CO_2)}H^{(CO_2)}$ $+ F_{202}/M^{(CaF_2)}H^{(CaF_2)} + F_{111}/M^{(CaSiO_3)}H^{(CaSiO_3)})$ $-(CONCPOR/141.94/3F_{109}^{(ROCK)}H^{(ROCK)} + F_{110}/M^{(SiO_2)}H_{110}^{(SiO_2)}$ $+ F_{165}/M^{(C)}H^{(C)} + \Sigma F_{200}^{(k)}/M^{(k)}H_{200}^{(k)} + F_{201}/M^{(H_2O)}H^{(H_2O)}) + F_{112}^{(P_2O_5)}Q_{out}$ $- Q_{EF} = 0$ where i = P_2O_5, H_2O; j = N_2, Ar, CO_2; k = N_2, Ar, CO_2, O_2
Enthalpy Function	$H_k^i(T) = (a_1^i + \frac{1}{2}a_2^iT + \frac{1}{3}a_3^iT^2 + \frac{1}{4}a_4^iT^3 + \frac{1}{5}a_5^iT^4 + \frac{b_1^i}{T})RT \quad J/mol$ i = H_2O, N_2, Ar, CO_2, O_2, SiO_2, C k = 110, 112, 151, 165, 166, 200, 201 $H^{(P_2O_5)} = (-1278.437)(1000) + 106.014(T - 298.15)J/mol$ Source: Lide (1982) $H^{(CaSiO_3)}(T) = -1584000 + 93(T - 298.15)J/mol$ Source: Felder and Roussleu (1986) $H^{(CaF_2)}(T) = ((-291.5)(1000) + 16.02(T - 298.15))(4.182)J/mol$ Source: Lide (1982) $H^{(ROCK)}(T) = (((-291.5)(1000) + (3)(-984.9)(1000)) + (16.02 + (3)(54.45))$ $(T - 298.15))(4.182) \quad J/mol$ Source: Lide (1982)

In Table 4-50, the overall material balance for the whole process is given with the mixture stream expressions. For the species material balance obtained using the reaction equations (4-48, 4-49, 4-50 and 4-51), the first equation is for the P_2O_5 balance; the second one is for the CO_2 generated from C balance; the third one is for the sand (SiO_2) balance; the fourth one is for the C balance; the fifth one is for the $CaSiO_3$ balance; the sixth one is for the oxygen balance; the seventh one is for the nitrogen balance; the eighth one is for the argon balance; the ninth one is for the carbon dioxide balance from the air input and output part; the tenth one is for the water balance; the eleventh one is for the CaF_2 balance, which is assumed to be inert in the whole process; the last one is for the impurity balance in the phosphate ore, which is assume as an inert in the whole process.

In the overall energy balance, Q_{EF} is the heat input for the electric furnace process in the form of steam and electrictiy, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in heat exchangers in the electric furnace based on unit product output, i.e. 10.2 MJ per lb of P_2O_5 (Austin, 1984). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 20 variables and 20 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 47 variables and 37 equations including the dependent overall material balance, so the number of degrees of freedom is 11.

C-2. HCl Digestion (Haifa Process) to Produce Phosphoric Acid (Slack, 1968; Baniel, et al., 1962; Baniel and Blumberg, 1959; Austin, 1984)

The capacity of Haifa process is set as the same as the wet process for phosphoric acid production, 3,833 TPD. This process use hydrochloric acid instead of sulfuric acid. The calcium chloride is soluble in phosphoric acid rather than precipitating as calcium sulfate (gypsum) does.

C-2-1. Process Description

The Israel Mining Industries (IMI) first developed the hydrochloric acid process for phosphoric acid production and has operated a demonstration plant in

Haifa since 1962 (Slack, 1968). This process has the advantage of using waste or by-product hydrochloric acid, where its disposal is often mandatory for expansion of the parent industry and for which sometimes it is very hard to find an outlet (Baniel, et al., 1962; Baniel and Blumberg, 1959).

Although the digestion of phosphate rock with hydrochloric acid produces phosphoric acid, the product acid includes the soluble byproducts, represented by calcium chloride, fluorine compounds and other impurities. The success of the process is determined by the ease that phosphoric acid can be separated from the highly soluble calcium chloride (Baniel, et al., 1962). Following the separation of solid impurities, the solution is contacted with butyl alcohol or isoamyl alcohol to selectively extract the phosphoric acid and hydrochloric acid, and leave the calcium chloride in the water layer, which is calcium chloride brine treated as a waste. Then, the acids enter the aqueous phase upon contact with demineralized water and separate as a solution of P_2O_5 and HCl. The mixture is then concentrated to phosphoric acid, and HCl in the exhaust vapor from the concentrator is recycled to the system (Slack, 1968). If the phosphate contains fluoride, hydrogen fluoride is either removed from the acid aqueous decomposition mixture prior to the solvent extraction, or extracted into the solvent together with the excess HCl and accompanies the latter when it is being separated from the phosphoric acid (Baniel and Blumberg, 1959).

The main reaction is as Equation 4-52. The block diagram is in Figure 4.17 with stream descriptions from Table 4-51.

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 20HCl = 10CaCl_2 + 6H_3PO_4 + 2HF \qquad (4\text{-}52)$$

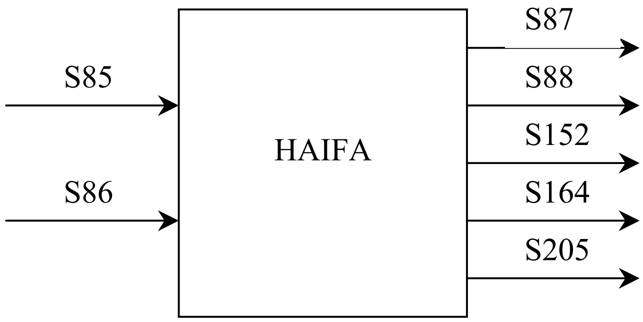


Figure 4.17 Block Diagram of Haifa Process

Table 4-51 Description of Haifa Process Streams

Name of Streams	Description
Input Streams	
S85	Phosphate rock to Haifa process
S86	HCl solution to Haifa process
Output Streams	
S87	Product H_3PO_4 from Haifa process
S88	Production of $CaCl_2$ in Haifa process
S152	Production of inert impurities from Haifa process
S164	Production of HF from Haifa process
S205	Production of water from Haifa process

C-2-2. Material Balance and Energy Balance

The parameters used in the material and energy balance of the Haifa Process are shown in Table 4-52 and the constraint equations are given in Table 4-53.

Table 4-52 Parameters in Haifa Proces, from Slack (1968) and Austin (1984)

Name	Meaning	Value
CONCPHCL	P_2O_5 concentration produced from Haifa process	0.54
CONCHCL	HCl concentration(weight fraction) to Haifa process	0.34
	Overall HCl conversion in Haifa process	1
	$CaF_2 \cdot 3Ca_3(PO_4)_2$ concentration in Haifa process	0.88

In Table 4-53, the overall material balance for the whole process is given with the mixture stream expressions. For the species material balance obtained using the

Table 4-53 Constraint Equations for Haifa Process

Material Balance

Overall

$$(F_{85} + F_{86}) - (F_{87} + F_{88} + F_{152} + F_{164} + F_{205}) = 0$$

where $F_{86} = F_{86}^{(HCl)} + F_{86}^{(H_2O)}$

$F_{87} = F_{87}^{(P_2O_5)} + F_{87}^{(H_2O)}$

Species

$$\text{HCl}: \frac{6}{(20)(36.46)} F_{86}^{(HCl)} - \frac{2}{141.94} F_{87}^{(P_2O_5)} = 0$$

$$\text{CaCl}_2: \frac{1}{(20)(36.46)} F_{86}^{(HCl)} - \frac{1}{(10)(110.98)} F_{88} = 0$$

$$\text{HF}: \frac{1}{(10)(110.98)} F_{88} - \frac{1}{(2)(20.01)} F_{164} = 0$$

$$\text{P}_2\text{O}_5: \frac{0.88}{1008.62} F_{85} - \frac{2}{(141.94)(6)} F_{87}^{(P_2O_5)} = 0$$

$$\text{H}_2\text{O}: F_{86}^{(H_2O)} - (F_{205} + F_{87}^{(H_2O)} - \frac{(3)(18.02)}{141.94} F_{87}^{(P\ O_5)}) = 0$$

Energy Balance

Overall

$$((F_{164}^{(HF)} / M^{(HF)} H_{164}^{(HF)} + F_{88}^{(CaCl_2)} / M^{(CaCl_2)} H_{88}^{(CaCl_2)} + \Sigma F_{87}^{(i)} / M^{(i)} H_{87}^{(i)}$$

$$+ F_{205} / M^{(H_2O)} H_{205}^{(H_2O)}) - (F_{86}^{(HCl)} / M^{(HCl)} H_{86}^{(HCl)} + F_{86}^{(H_2O)} / M^{(H_2O)} H_{86}^{(H_2O)}$$

$$+ 0.88 F_{85} / M^{(ROCK)} H_{85}^{(ROCK)})) - Q_{CH} = 0$$

where i = H_2O, P_2O_5

Enthalpy Function

$$H_k^i(T) = (a_1^i + \frac{1}{2} a_2^i T + \frac{1}{3} a_3^i T^2 + \frac{1}{4} a_4^i T^3 + \frac{1}{5} a_5^i T^4 + \frac{b_1^i}{T}) RT \quad \text{J/mol}$$

i = H_2O, $CaCl_2$, HF

k = 86, 87, 88, 164, 205

$$H^{(P_2O_5)} = (-1278.437)(1000) + 106.014(T - 298.15) \text{J/mol}$$

Source: Lide (1982)

$$H^{(ROCK)}(T) = (((-291.5)(1000) + (3)(-984.9)(1000)) + (16.02 + (3)(54.45))$$

$$(T - 298.15))(4.182) \qquad \text{J/mol}$$

Source: Lide (1982)

$$H^{(HCl)} = (-98.34)(1000) + 73.993(T - 298.15) + \frac{1}{2}(-12946E-01)$$

$$(T^2 - 298.15^2) + \frac{1}{3}(-7.8980E-05)(T^3 - 298.15^3) + \frac{1}{4}(2.6409E-06)$$

$$(T^4 - 298.15^4)$$

Source: Yaws (1999)

reaction equations (4-52), the first equation is for the HCl balance; the second one is for the $CaCl_2$ balance; the third one is for the HF balance; the fourth one is for the P_2O_5 balance; the last one is for the H_2O balance.

In the overall energy balance, Q_{CH} is the heat input for Haifa process in the form of steam in the heat exchanger, which is calculated from the energy balance. In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 11 variables and 10 equations, so the number of degrees of freedom is 1. For the material and energy balance, there are 26 variables and 19 equations, so the number of degrees of freedom is 7.

C-3. Gypsum Reuse - Sulfur and Sulfur Dioxide Recovery (Paisley, 2000; Kosyl'kov and Rogachev, 1983; Campbell and Fisher, 1971)

The gypsum produced from wet process for phosphoric acid production can be reused to recover sulfur and sulfur dioxide. There are two processes, one is sulfur dioxide recovery; and the other is sulfur and sulfur dioxide recovery. Neither process is commercialized now because of sulfur from other sources and process energy requirements. These two processes are incorporated in the chemical complex, and they may become important in the future.

C-3-1. Sulfur Dioxide Recovery from Gypsum (Paisley, 2000; Kosyl'kov and Rogachev, 1983)

The capacity of this process was set to be 1,970,000 metric tons per year of SO_2, which is based on the consuming all of gypsum produced from the wet process for phosphoric acid.

C-3-1-1. Process Description

Crushed waste gypsum is dried and dehydrated to anhydride in a dryer or calciner (Equation 4-53). Then the anhydride is reduced to CaS by means of a reducing agent such as a medium BTU wood gas whose composition is in Table 4-54. The reactions of CO, H_2 and CH_4 are shown in Equation 4-54, 4-55 and 4-56. The preferred temperature for reducing the calcium sulfate is about $1{,}500\,^{\circ}\mathrm{F}$ to about $1{,}600\,^{\circ}\mathrm{F}$. CH_4 conversion is 56%.

After separating CaS from the gaseous by-products of the reactions, CaS is oxidized with air to produce calcium oxide and sulfur dioxide that is the feed to the sulfuric acid plant (Equation 4-57) (Paisley, 2000). The block diagram is Figure 4.18 with stream description in Table 4-55.

$$\mathrm{CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 + 2H_2O} \qquad \text{Dehydration} \quad (4\text{-}53)$$

$$\mathrm{CaSO_4 + 4CO \rightarrow CaS + 4CO_2} \qquad \text{Reduction} \quad (4\text{-}54)$$

$$\mathrm{CaSO_4 + 4H_2 \rightarrow CaS + 4H_2O} \qquad \text{Reduction} \quad (4\text{-}55)$$

$$\mathrm{CaSO_4 + CH_4 \rightarrow CaS + CO_2 + 2H_2O} \qquad \text{Reduction} \quad (4\text{-}56)$$

$$\mathrm{CaS + O_2 + CaSO_4 \rightarrow 2CaO + 2SO_2} \qquad \text{Oxidation} \quad (4\text{-}57)$$

Figure 4.18 Block Diagram of SO_2 Recovery Plant

Table 4-54 Parameters in Sulfur Dioxide Recovery from Gypsum, from Paisley (2000)

Parameters		
CH_4 conversion		0.56
CO conversion		1
H_2 conversion		1
Wood gas composition (Volume %)		
	H_2	17.76
	CO	50.09
	CO_2	9.88
	CH_4	16.76
	C_2H_6	5.51

Table 4-55 Description of Process Streams in SO_2 Recovery Plant

Name of Streams	Description
Input Streams	
S400	Gypsum to sulfur dioxide recovery plant
S401	Wood gas to sulfur dioxide recovery plant
S402	Air to sulfur dioxide recovery plant
Output Streams	
S403	Vent gas from sulfur dioxide recovery plant
S404	Cao produced from sulfur dioxide recovery plant
S405	SO_2 produced from sulfur dioxide recovery plant
S406	Water produced from sulfur dioxide recovery plant

C-3-1-2. Material Balance and Energy Balance

Using the parameters in Table 4-54 the material balance and energy balance of the SO_2 recovery plant are given in Table 4-56.

In Table 4-56, the overall material balance for the whole process is given with the mixture stream expressions. For the species material balance obtained using the reaction equations (4-53, 4-54, 4-55, 4-56 and 4-57), the first equation is for the crystal water balance from the gypsum; the second one is for the water balance produced from the reactions; the third one is for the gypsum balance; the fourth one is for the CaO balance; the fifth one is for the SO_2 balance; the sixth one is for the O_2

balance; the seventh one is for CH_4 balance; the eighth one is for the Ar balance; the ninth one is for CO_2 balance; the tenth one is for the N_2 balance; the last one is for the C_2H_6 balance.

Table 4-56 Constraint Equations for Sulfur Dioxide Recovery from Gypsum

Material Balance	
Overall	$(F_{400}+F_{401}+F_{402})-(F_{403}+F_{404}+F_{405}+F_{406})=0$ where $F_{401}=F_{401}^{(H_2)}+F_{401}^{(CO)}+F_{401}^{(CO_2)}+F_{401}^{(CH_4)}+F_{401}^{(C_2H_6)}$ $F_{402}=F_{402}^{(O_2)}+F_{402}^{(N_2)}+F_{402}^{(CO_2)}+F_{402}^{(Ar)}$ $F_{403}=F_{403}^{(N_2)}+F_{403}^{(Ar)}+F_{403}^{(CO_2)}+F_{403}^{(CH_4)}+F_{403}^{(C_2H_6)}+F_{403}^{(H_2O)}$
Species	H_2O-1: $\frac{(2)(18.02)}{172.18}F_{400}-F_{406}=0$
	H_2O-2: $\frac{(2)(0.56)}{16.05}F_{401}^{(CH_4)}+\frac{1}{2.02}F_{401}^{(H_2)}-\frac{1}{18.02}F_{403}^{(H_2O)}=0$
	Gypsum: $\frac{1}{172.18}F_{400}-\frac{0.5}{56.08}F_{404}-(\frac{1}{(28.01)(4)}F_{401}^{(CO)}+\frac{1}{(2.02)(4)}F_{401}^{(H_2)}$ $+\frac{0.56}{16.05}F_{401}^{(CH_4)})=0$
	CaO: $\frac{1}{56.08}F_{404}-\frac{1}{172.18}F_{400}=0$
	SO_2: $\frac{1}{172.08}F_{400}-\frac{1}{64.06}F_{405}=0$
	O_2: $\frac{1}{32}F_{402}^{(O_2)}-\frac{0.5}{56.08}F_{404}=0$
	CH_4: $(1-0.56)F_{401}^{(CH_4)}-F_{403}^{(CH_4)}=0$
	Ar: $F_{403}^{(Ar)}-F_{402}^{(Ar)}=0$
	CO_2: $F_{403}^{(CO_2)}-(\frac{44.01}{28.01}F_{401}^{(CO)}+\frac{(0.56)(44.01)}{16.05}F_{401}^{(CH_4)}+F_{402}^{(CO_2)}+F_{401}^{(CO_2)})=0$
	N_2: $F_{403}^{(N_2)}-F_{402}^{(N_2)}=0$
	C_2H_6: $F_{403}^{(C_2H_6)}-F_{401}^{(C_2H_6)}=0$
Energy Balance	
Overall	$(\Sigma F_{403}^{(i)}/M^{(i)}H_{403}^{(i)}+F_{404}/M^{(CaO)}H_{404}^{(CaO)}+F_{405}/M^{(SO_2)}H_{405}^{(SO_2)}$ $+F_{406}/M^{(H_2O)}H_{406}^{(H_2O)})-(F_{400}/M^{(GYP)}H_{400}^{(GYP)}+\Sigma F_{401}^{(j)}/M^{(j)}H_{401}^{(j)}$ $+\Sigma F_{402}^{k}/M^{(k)}H_{402}^{(k)})+Q_{out}F_{400}-Q_{SR}=0$

Table 4-56 Continued

Energy Balance (Continued)	
Overall	i = CO_2, N_2, Ar, H_2O, CH_4, C_2H_6; j = CO_2, CH_4, C_2H_6, H_2, CO; k = CO_2, N_2, Ar, O_2
Enthalpy Function	$H^i_k(T) = (a^i_1 + \frac{1}{2}a^i_2 T + \frac{1}{3}a^i_3 T^2 + \frac{1}{4}a^i_4 T^3 + \frac{1}{5}a^i_5 T^4 + \frac{b^i_1}{T})RT$ J/mol i = CO_2, N_2, Ar, H_2O, CH_4, C_2H_6, H_2, CO, O_2, CaO, SO_2, k = 401, 402, 403, 404, 405, 406 $H^{(GYP)}_k(T) = ((-483.42)(1000) + (44.46)(T - 298.15))(4.182)$ J/mol k=400 Source: Lide (1982).

In the overall energy balance, Q_{SR} is heat input of the SO_2 recovery from gypsum plant in the form of steam in heat exchanger, heater and dryer, which is calculated from the energy balance. Q_{out} is heat output removed by cooling water in heat exchanger and condenser in the SO_2 recovery from gypsum plant based on the unit of gypsum feedstock, 2.2 MJ per lb of gypsum (Kosyl'kov and Rogachev, 1983). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 22 variables and 22 equations including the dependent overall mass balance, so the number of degrees of freedom is 1. For the material and energy balance, there are 49 variables and 42 equations including the dependent overall mass balance, so the number of degrees of freedom is 8.

C-3-2. Sulfur and Sulfur Dioxide Recovery from Gypsum (Campbell and Fisher, 1971; Kosyl'kov and Rogachev, 1983)

The capacity of this process was set to be 988,000 metric tons per year of S, which is based on the consuming all of gypsum produced from the wet process for phosphoric acid.

C-3-2-1. Process Description

Crushed gypsum, having particle sizes within the approximately range of 0.25-1.50 inch, is first dehydrated by heating (Equation 4-58) (Campbell and Fisher, 1971).

$$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 + 2H_2O \tag{4-58}$$

Secondly, the dehydrated calcium sulfate is reacted with the reducing gas (Equation 4-59, 4-60, 4-61 and 4-62).

$$CaSO_4 + 4CO \rightarrow CaS + 4CO_2 \tag{4-59}$$

$$CaSO_4 + 4H_2 \rightarrow CaS + 4H_2O \tag{4-60}$$

$$CaSO_4 + H_2 \rightarrow CaO + SO_2 + H_2O \tag{4-61}$$

$$CaSO_4 + CO \rightarrow CaO + SO_2 + CO_2 \tag{4-62}$$

Then the gas product contains SO_2, CO_2 and H_2O. The SO_2 is separated and becomes the feed to sulfuric acid plant. The reactor product CaO and CaS are quenched in water, ground to a fine slurry and carried to a gas-liquid reactor where it reacts with CO_2 supplied by the recover gas stream from a later stage in the process, and the reactions are the following Equations (4-63, 4-64 and 4-65).

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{4-63}$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \tag{4-64}$$

$$CaS + H_2O + CO_2 \rightarrow CaCO_3 + H_2S \tag{4-65}$$

To convert the gaseous product H_2S to elemental sulfur, the conventional Claus process is employed with additional air input according to the following Equations (4-7 and 4-8).

$$H_2S + 1.5O_2 \rightarrow SO_2 + H_2O \tag{4-7}$$

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O \tag{4-8}$$

The block diagram is Figure 4.19 with stream description in Table 4-57.

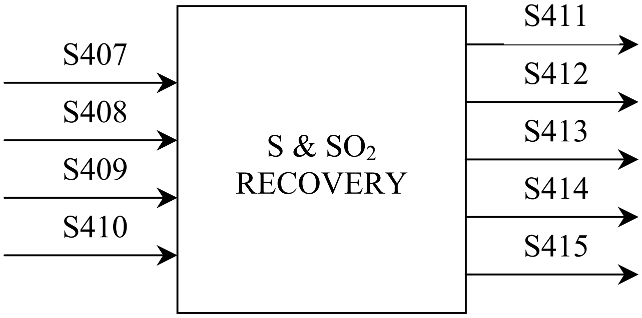


Figure 4.19 Block Diagram of S and SO_2 Recovery Plant

Table 4-57 Description of Process Streams in S and SO_2 recovery Plant

Name of Streams	Description
Input Streams	
S407	Reducing gas to sulfur and sulfur dioxide recovery plant
S408	Gypsum to sulfur and sulfur dioxide recovery plant
S409	H_2O to sulfur and sulfur dioxide recovery plant
S410	Air to sulfur and sulfur dioxide recovery plant
Output Streams	
S411	SO_2 generated from sulfur and sulfur dioxide recovery plant
S412	Sulfur generated from sulfur and sulfur dioxide recovery plant
S413	Vent generated from sulfur and sulfur dioxide recovery plant
S414	$CaCO_3$ generated from sulfur and sulfur dioxide recovery plant
S415	H_2O generated from sulfur and sulfur dioxide recovery plant

C-3-2-2. Material Balance and Energy Balance

Using the parameters in Table 4-58 the material balance and energy balance of the S and SO_2 recovery plant are given in Table 4-59.

In Table 4-59, the overall material balance for the whole process is given with the mixture stream expressions. For the species material balance obtained using the reaction equations (4-7, 4-8, 4-58, 4-59, 4-60, 4-61, 4-62, 4-63, 4-64 and 4-65), the first equation is for the $CaCO_3$ balance; the second one is for the SO_2 balance; the third one is for the H_2 balance; the fourth one is for the S balance; the fifth one is for the gypsum balance; the sixth one is for the H_2O balance; the seventh one is for the CO_2 balance; the eighth one is for the O_2 balance; the ninth one is for N_2 balance; the last one is for the Ar balance.

Table 4-58 Parameters in S and SO_2 Recovery from Gypsum Plant, from Campbell and Fisher (1971)

Parameters		
Ratio of Slurry water to gypsum		420:100
Ratio of H_2 and CO for CaO to those for CaS		1:8
Reduce gas composition (Volume %)		
	H_2	39.5
	CO	39.5
	H_2O	13.2
	CO_2	7.8

In the overall energy balance, Q_{SSR} is heat input of the S and SO_2 recovery from gypsum plant in the form of steam in heat exchanger and heater, which is calculated from the energy balance. Q_{out1} is one part of heat output removed by cooling water in heat exchanger and condenser in the S and SO_2 recovery plant based on the unit of SO_2 product, 6 MJ per lb of SO_2 (Kosyl'kov and Rogachev, 1983). Q_{out2} is another part of heat output removed by cooling water in heat exchanger and condenser in the S and SO_2 recovery plant based on the unit of S product, 8.6 MJ per lb of S (Kosyl'kov and Rogachev, 1983). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 20 variables and 20 equations including the dependent overall mass balance, so the number of degrees of freedom is 1. For the

Table 4-59 Constraint Equations for S and SO_2 Recovery from Gypsum Plant

Material Balance

Overall

$$(F_{407}+F_{408}+F_{409}+F_{410})-(F_{411}+F_{412}+F_{413}+F_{414}+F_{415})=0$$

$$\text{where } F_{407}=F_{407}^{(H_2)}+F_{407}^{(CO)}+F_{407}^{(CO_2)}+F_{407}^{(H_2O)}$$

$$F_{410}=F_{410}^{(O_2)}+F_{410}^{(N_2)}+F_{410}^{(CO_2)}+F_{410}^{(Ar)}$$

$$F_{413}=F_{413}^{(N_2)}+F_{413}^{(Ar)}+F_{413}^{(CO_2)}$$

Species

$$CaCO_3\text{: } \frac{1}{172.18}F_{408}-\frac{1}{100.09}F_{414}=0$$

$$SO_2\text{: } \frac{1}{(2.02)(9)}F_{407}^{(H_2)}+\frac{1}{(28.01)(9)}F_{407}^{(CO)}-\frac{1}{64.06}F_{411}=0$$

$$H_2\text{: } \frac{8}{(2.02)(9)(4)}F_{407}^{(H_2)}+\frac{8}{(28.01)(9)(4)}F_{407}^{(CO)}-\frac{1}{32.06}F_{412}=0$$

$$S\text{: } \frac{1}{172.18}F_{408}-(\frac{1}{64.06}F_{411}+\frac{1}{32.06}F_{412})=0$$

$$\text{Gypsum: } \frac{100}{18.02}F_{409}-\frac{420}{172.18}F_{408}=0$$

$$H_2O\text{: } F_{407}^{(H_2O)}+\frac{(18.02)(2)}{172.18}F_{408}+\frac{18.02}{2.02}F_{407}^{(H_2)}+F_{409}-F_{415}=0$$

$$CO_2\text{: } F_{407}^{(CO_2)}+\frac{44.01}{28.01}F_{407}^{(CO)}-\frac{44.01}{100.09}F_{414}+F_{410}^{(CO_2)}-F_{413}^{(CO_2)}=0$$

$$O_2\text{: } \frac{1}{32}F_{410}^{(O_2)}-\frac{0.5}{32.06}F_{412}=0$$

$$N_2\text{: } F_{413}^{(N_2)}-F_{410}^{(N_2)}=0$$

$$Ar\text{: } F_{413}^{(Ar)}-F_{410}^{(Ar)}=0$$

Energy Balance

Overall

$$(F_{411}/M^{(SO_2)}H_{411}^{(SO_2)}+F_{412}/M^{(S)}H_{412}^{(S)}+\Sigma F_{413}^{(i)}/M^{(i)}H_{413}^{(i)}$$

$$+F_{414}/M^{(CaCO_3)}H_{414}^{(CaCO_3)}+F_{415}/M^{(H_2O)}H_{415}^{(H_2O)})-(\Sigma F_{407}^{(j)}/M^{(j)}H_{407}^{(j)}$$

$$+F_{408}/M^{(GYP)}H_{408}^{(GYP)}+F_{409}/M^{(H_2O)}H_{409}^{(H_2O)}+\Sigma F_{410}^{(k)}/M^{(k)}H_{410}^{(k)})+Q_{out1}F_{411}$$

$$+Q_{out2}F_{412}-Q_{SSR}=0$$

i = N_2, CO_2, Ar; j = CO_2, H_2, CO, H_2O; k = N_2, CO_2, Ar, O_2

Enthalpy Function

$$H_k^i(T)=(a_1^i+\frac{1}{2}a_2^iT+\frac{1}{3}a_3^iT^2+\frac{1}{4}a_4^iT^3+\frac{1}{5}a_5^iT^4+\frac{b_1^i}{T})RT \quad \text{J/mol}$$

i = CO_2, N_2, Ar, H_2O, H_2, CO, O_2, SO_2, S, $CaCO_3$

k = 407, 409, 410, 411, 412, 413, 414, 415

$$H_k^{(GYP)}(T)=((-483.42)(1000)+(44.46)(T-298.15))(4.182) \qquad \text{J/mol}$$

k=408; Source: Lide (1982).

material and energy balance, there are 47 variables and 38 equations including the dependent overall mass balance, so the number of degrees of freedom is 10.

C-4. Acetic Acid (New Process) (Taniguchi, et al., 1998; Zerella, et al., 2003; Indala, 2004; Louisiana Chemical & Petroleum Products List, 1998)

There are two acetic acid processes in the chemical complex superstructure, one is conventional acetic acid plant where acetic acid produced from methanol and carbon monoxide in the base case; and the other is a potentially new acetic acid plant which uses methane and carbon dioxide as feedstock. The detailed description of the new process is given below.

The production capacity of this process was selected to be 8,180 metric tons per year (Indala, 2004). This is based on the Dow Chemical Company, an acetic acid plant located in Hahnville, LA, with the production capacity of 18 million pouns per year (8,160 metric tons per year) (Louisiana Chemical & Petroleum Products List, 1998).

C-4-1. Process Description

Acetic acid can be made by direct conversion of carbon dioxide and methane to acetic acid (Equation 4-66) (Taniguchi, et al., 1998; Zerella, et al., 2003). The block diagram is shown in Figure 4.20 with the stream definitions in Table 4-60.

$$CO_2 + CH_4 = CH_3COOH \qquad \Delta H^\circ = 36 \text{ KJ/mol} \qquad (4\text{-}66)$$

Figure 4.20 Block Diagram of New Acetic Acid Plant

Table 4-60 Description of Process Streams in New Acetic Acid Plant

Name of Streams	Description
Input Streams	
S700	CO_2 to new acetic acid plant
S701	Natural gas to new acetic acid plant
Output Streams	
S702	Production of acetic acid from new acetic acid plant

C-4-2. Material Balance and Energy Balance

Using the parameters in Table 4-61 the material balance and energy balance of new acetic acid plant are shown in Table 4-62.

In Table 4-62, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equation (4-66), the first equation is for the CO_2 balance; and the second one is for the CH_4 balance.

In the overall energy balance, Q_{AA2} is heat input of the new acetic acid plant in the form of steam in heat exchanger to supply the heat needed for the endothermic reaction (Equation 4-66) and distillation column reboiler for heating reactants and product separation, which is calculated from the energy balance. Q_{out} is heat output removed by cooling water in heat exchanger and distillation column condenser for cooling reactants and product separation in the new acetic acid plant, based on the unit of acetic acid product, 558 KJ per lb of acetic acid (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 3 variables and 3 equations including the dependent overall mass balance, so the number of degrees of freedom is 1. For the material and energy balance, there are 10 variables and 7 equations including the dependent overall mass balance, so the number of degrees of freedom is 4.

Table 4-61 Parameters in New Acetic Acid Production

Name	Meaning	Value
	CO_2 utilization	1.0
	CH_4 utilization	1.0

Table 4-62 Constraint Equations for New Acetic Acid Production

Material Balance	
Overall	$F_{700} + F_{701} - F_{702} = 0$
Species	CO_2: $\frac{1}{44.01}F_{700} - \frac{1}{60.06}F_{702} = 0$
	CH_4: $\frac{1}{16.05}F_{701} - \frac{1}{60.06}F_{702} = 0$
Energy Balance	
Overall	$F_{702}^{(aceticacid)} / M^{(aceticacid)} H_{702}^{(aceticacid)} - (F_{700}^{(CO_2)} / M^{(CO_2)} H_{700}^{(CO_2)}$ $+ F_{701}^{(CH_4)} / M^{(CH_4)} H_{702}^{(CH_4)}) + Q_{out} F_{702}^{(aceticacid)} - Q_{AA2} = 0$
Enthalpy Function	$H_k^i(T) = (a_1^i + \frac{1}{2}a_2^i T + \frac{1}{3}a_3^i T^2 + \frac{1}{4}a_4^i T^3 + \frac{1}{5}a_5^i T^4 + \frac{b_1^i}{T})RT$ J/mol $i = CO_2, CH_4$; $k = 700, 701$ $H_k^{(aceticacid)}(T) = ((-115.8)(1000) + (29.7)(T - 298.15))(4.185)$ J/mol k=702 Source: Lide (1982).

C-5. Ethylbenzene (EB) Dehydrogenation with CO_2 to Styrene (New Styrene Process) (Sakurai, et al., 2000; Chang, et al., 1998; Indala, 2004; Mimura, et al., 1998; Louisiana Chemical & Petroleum Products List, 1998)

There are several potentially new processes that use CO_2 for the production of styrene available (Sakurai, et al., 2000; Chang, et al., 1998; Mimura, et al., 1998). After detailed comparison using HYSYS simulation and economic evaluation (Indala, 2004), a potentially new styrene process by Mimura, et al. (1998) was integrated into the chemical complex. The capacity of this process is set to be 362,000 metric tons per year. For styrene production, the production rate of Deltech Corporation in Baton Rouge plant, 800 million pounds per year (362,000 metric tons per year), was used in the superstructure (Louisiana Chemical & Petroleum Products List, 1998).

C-5-1. Process Description

A new method for the production of styrene through dehydrogenation of ethylbenzene in the presence of carbon dioxide was described by Mimura, et al. (1998). The Fe/Ca/Al oxides catalyst exhibited high activity in the presence of CO_2. The reactor operated at 580°C and 1 atm pressure. The ratio of CO_2 to EB in the feedstock input is 9:1. The observed yield of styrene was 70%, and the selectivity to styrene was 100%. The following reaction occurs in the reactor.

$$C_6H_5\text{-}C_2H_5 + CO_2 \rightarrow C_6H_5\text{-}C_2H_3 + CO + H_2O \tag{4-67}$$

The block diagram of new styrene process is in Figure 4.21 with the stream description in Table 4-63.

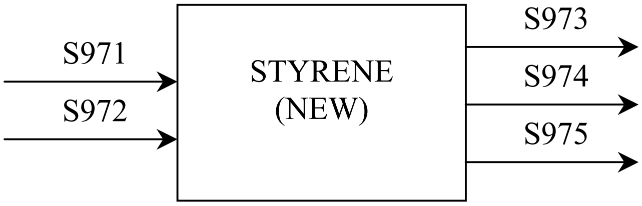


Figure 4.21 Block Diagram of New Styrene Process

C-5-2. Material Balance and Energy Balance

Using the parameters in Table 4-64, the material and energy balances of new styrene process are given in Table 4-65.

In Table 4-65, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equations (4-67), the first equation is for the CO balance; and the second one is for the H_2O balance; the third one is for the CO_2 balance; the last one is for the EB balance.

Table 4-63 Description of the Streams in New Styrene Process

Stream Name	Stream Description
Input Streams	
S971	Ethylbenzene to new styrene process
S972	Carbon dioxide to new styrene process
Output Streams	
S973	Carbon monoxide produced from new styrene process
S974	Styrene produced from new styrene process
S975	Water produced from new styrene plant

In the overall energy balance, Q_{NSTYB} is heat input in the form of steam in heat exchanger to supply the heat for the endothermic reaction and product separation of the new styrene process, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in heat exchanger and condenser for product separation in the new styrene process based on the unit of styrene product, 3 MJ per lb of styrene (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 5 variables and 5 equations including one dependent one (overall material balance), so the number of degrees of freedom is 1. For the material and energy balances, there are 16 variables and 11 equations including one dependent one (overall material balance), so the number of degrees of freedom is 6.

Table 4-64 Parameters in New Styrene Process

Name	Meaning	Value
	Conversion of EB in new styrene process	100%
	Selectivity of EB to styrene in new styrene process	100%

Table 4-65 Constraint Equations for New Styrene Process

Material Balance	
Overall	$(F_{971}+F_{972})-(F_{973}+F_{974}+F_{975})=0$
Species	CO: $\frac{F_{973}}{mw(CO)}-\frac{F_{974}}{mw(styrene)}=0$ H_2O: $\frac{F_{975}}{mw(H_2O)}-\frac{F_{974}}{mw(styrene)}=0$ CO_2: $\frac{F_{974}}{mw(styrene)}-\frac{F_{972}}{mw(CO_2)}=0$ EB: $\frac{F_{974}}{mw(styrene)}-\frac{F_{971}}{mw(EB)}=0$
Energy Balance	
Overall	$(F_{973}^{(CO)}/M^{(CO)}H_{973}^{(CO)}+F_{974}^{(STYRENE)}/M^{(STYRENE)}H_{974}^{(STYRENE)}$ $+F_{975}^{(H_2O)}/M^{(H_2O)}H_{975}^{(H_2O)})-(F_{971}^{(EB)}/M^{(EB)}H_{971}^{(EB)}+F_{972}^{(CO_2)}/M^{(CO_2)}H_{972}^{(CO_2)})$ $+Q_{out}F_{974}^{(STYRENE)}-Q_{NSTYB}=0$
Enthalpy Function	$H_k^i(T)=(a_1^i+\frac{1}{2}a_2^iT+\frac{1}{3}a_3^iT^2+\frac{1}{4}a_4^iT^3+\frac{1}{5}a_5^iT^4+\frac{b_1^i}{T})RT$ J/mol $i = CO_2, CO, H_2O$ $k = 972, 973, 975$ $H_{1071}^{(EB)}=-12300+185.572(T-298.15)$ J/mol Source: Lide (1990) and NIST (2002) $H_{1072}^{(STYRENE)}=103400+183.2(T-298.15)$ J/mol Source: NIST (2002)

C-5-3. Comparison between Conventional and New Styrene Processes

Mimura, et al. (1998) gave a detailed comparison between the conventional and potentially new styrene processes. On one hand the potentially new process would operate at 580°C whereas the conventional process operates at over 630°C. On the other hand, the energy requirement in the new styrene process (about 6.3 x 10^8 cal/t-styrene) could be much lower than that for the conventional process (about 1.5 x 10^9 cal/t-styrene), mainly because a large quantity of latent heat of water condensation cannot be recovered in the conventional process. In general, the potentially new styrene process using CO_2 with lower reaction temperature would have lower energy requirement compared to the existing conventional process.

C-6. Methanol (New Processes) (Pellegrino, 2000; Inui, 2002; Nerlov and Chorkendorff, 1999; Omata, et al., 2002; Toyir, et al., 1998; Sahibzada, et al., 1998; Ushikoshi, et al., 1998; Nomura, et al., 1998; Jun, et al., 1998; Mabuse, et al., 1998; Fukui, et al., 1998; Hara, et al., 1998a; Bill, et al., 1998; Bonivardi, et al., 1998; Hirano, et al., 1998; Indala, 2004; Louisiana Chemical & Petroleum Products List, 1998)

Pellegrino (2000) reported that methanol is in the list developed by Pacific Northwest National Laboratory (PNNL) with a potential energy savings of 37 trillion BTUs per year through improved catalysts. The conventional processes for methanol include production from synthesis gas. Following is a summary of experimental studies that use carbon dioxide to produce methanol.

Inui (2002) described four ways for the synthesis of methanol by CO_2 hydrogenation using multifunctional catalysts (Cu-Zn-Cr-Al mixed oxide) at different temperature and pressure (Equation 4-68). However, the conversions and selectivities are low in the experimental studies, and they require more hydrogen than that required in the conventional process. The catalysts used in these studies were not commercial catalysts (Cu-Zn-Cr mixed oxide) for methanol production.

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H^o = -49 \text{ KJ/mol}, \Delta G^o = 3 \text{ KJ/mol} \quad (4\text{-}68)$$

Nerlov and Chorkendorff (1999) described a laboratory scale process for the synthesis of methanol from CO_2 and H_2 over Cu(100) catalysts at 543K and 1.5 atm (Equation 4-68). They also reported the use of Ni/Cu(100) catalyst operated at the same temperature and pressure but the reaction mixture contained CO, CO_2 and H_2 (Equation 4-68 and 4-22).

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H^o = -41\ KJ/mol,\ \Delta G^o = -29\ KJ/mol \quad (4\text{-}22)$$

Omata, et al. (2002) described methanol synthesis from CO_2-containing synthesis gas over Cu-Mn catalysts supported on $ZnrO_2$ and TiO_2 in a flow type fixed bed reactor at 250°C and 10 atm (Equation 4-68 and 4-22).

Toyir, et al. (1998) gave the methanol synthesis method from CO_2 hydrogenation over Raney Cu-Zr catalyst leached with aqueous solution of zincate (NaOH + ZnO) in a flow reactor at a temperature of 523K and at a pressure of 50 atm (Equation 4-68 and 4-32). The ratio of hydrogen to carbon dioxide in the feed was 3:1 and the space velocity was 18000 h^{-1}.

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta H^o = 41\ KJ/mol,\ \Delta G^o = 29\ KJ/mol \quad (4\text{-}32)$$

Sahibzada, et al. (1998) described a laboratory methanol process from CO_2 and H_2 over Pd promoted $Cu/ZnO/Al_2O_3$ catalysts in an internal recycle reactor (300 cm^3 volume, 100cm^3 catalyst basket) at 250°C and 5 MPa (Equation 4-68 and 4-32). The ratio of hydrogen to carbon dioxide in the feed gas was 4:1.

Ushikoshi, et al. (1998) reported a pilot methanol plant from CO_2 and H_2 over a multi-component catalyst ($Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3$) at 523 K and 5 MPa (Equation 4-68, 4-32 and 4-34). The ratio of hydrogen to carbon dioxide in the feed gas was 3:1.

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H^o = -90.8\ KJ/mol \quad \Delta G^o = -25\ KJ/mol \qquad (4\text{-}34)$$

Nomura, et al. (1998) described the hydrogenation of carbon dioxide over Fe promoted Cu based catalysts. Fe-CuO-ZnO/TiO_2 catalyst was used in this research. The reaction was carried out at 553 K, 1 MPa (10 atm), and W/F_{CO2} = 570 kg-cat-s/mol. The ratio of hydrogen to CO_2 in the feed gas was 4:1.

Jun, et al. (1998) reported hydrogenation of CO_2 for methanol and dimethyl ether over hybrid catalyst of Cu/ZnO/Cr_2O_3 and CuNaY zeolite at 523K and 30atm (Equation 4-68, 4-34 and 4-69). The feed gas composition of H_2 to CO_2 was 3:1.

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H^o = -24 \text{ KJ/mol } \Delta G^o = -17 \text{ KJ/mol} \quad (4\text{-}69)$$

Mabuse, et al. (1998) described the liquid-phase methanol synthesis from CO_2 and H_2 over Cu/ZnO-based multicomponent catalyst (Cu/ZnO/ZrO_2/Al_2O_3) modified with special silicone oil (5 wt%) at 523K and 15 MPa (Equation 4-68). The ratio of hydrogen to carbon dioxide in the feed gas was 3:1.

Fukui, et al. (1998) described methanol production from hydrogenation of carbon dioxide over Cu/ZnO catalysts at 250°C and 5 MPa (Equation 4-68).

Hara, et al. (1998a) presented a laboratory process for the synthesis of gasoline from carbon dioxide via methanol as an intermediate over a Pd-modified composite catalyst (38.1% Cu, 29.4% ZnO, 1.6% Cr_2O_3, 13.1% Al_2O_3, 17.8% Ga_2O_3) at 270°C and 80 atm. The feed gas was a CO_2 rich gas with composition CO_2/CO/H_2 equal to 22/3/75.

Bill, et al. (1998) described two different methods of CO_2 hydrogenation for methanol production. The first one was in a conventional tubular packed-bed reactor filled with copper based catalyst (CuO/ZnO/Al_2O_3) at 220°C and 20 bar with the feed gas composition H_2/CO_2 = 3:1. The second one uses a dielectric-barrier discharge (DBD) with the aid of a catalyst inside the discharge space at less than 100°C.

Bonivardi, et al. (1998) described a new methanol production method from CO_2 hydrogenation over Ca promoted Pd/SiO_2 catalyst in a copper-plated differential microreactor at 523 K and 3 MPa. The ratio of H_2 to CO_2 in the feed gas was 3:1. The selectivity to methanol was more than 95% (Equation 4-32 and 4-34).

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta H^o = 41 \text{ KJ/mol}, \Delta G^o = 29 \text{ KJ/mol} \qquad (4\text{-}32)$$

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H^o = -90.8 \text{ KJ/mol}, \Delta G^o = -25 \text{ KJ/mol} \qquad (4\text{-}34)$$

Hirano, et al. (1998) described a laboratory process of carbon dioxide hydrogenation for methanol production over $CuO\text{-}ZnO\text{-}Al_2O_3$ catalyst (Al_2O_3 5 wt%) at 513-521 K and 9 MPa with a feed gas composition of H_2/CO_2 = 3/1.

However, not all of the above experimental studies for methanol from carbon dioxide hydrogenation are competitive with the conventional process. Only four new methanol processes (Bonivardi, et al., 1998; Jun, et al., 1998; Nerlov and Chorkendorff, 1999; Ushikoshi, et al., 1998) were selected for process design using HYSYS which is discussed in the next section (Indala, 2004).

The production capacity of these four processes was based on a methanol plant of Ashland Chemical Inc., located in Plaquemine, LA, with the production rate of 160 million gallons per year (480,000 metric tons per year) (Louisiana Chemical & Petroleum Products List, 1998).

C-6-1. New Methanol (Bonivardi) Process (Bonivardi, et al., 1998; Indala, 2004; Louisiana Chemical & Petroleum Products List, 1998)

C-6-1-1. Process Description

Bonivardi, et al. (1998) described a new methanol production method from CO_2 hydrogenation over Ca promoted Pd/SiO_2 catalyst. The reaction was carried out in a copper-plated differential microreactor at 523 K and 3 MPa with a space velocity of 10000 h^{-1}. The ratio of H_2 to CO_2 in the feed gas was 3:1. The observed rate of synthesis of methanol was 50×10^{-8} mol/gPd-s. The selectivity to methanol was more than 95%.

The reaction mechanism was given that methanol was not directly formed through the CO_2 reaction, but it was produced through formation of CO and its consecutive hydrogenation to methanol (Equation 4-32 and 4-34) (Bonivardi, et al., 1998). Large recycle ratios were employed to maintain the selectivity to methanol if the process is commercialized (Bonivardi, et al., 1998). The reactions occurring in this study are:

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta H^o = 41 \text{ KJ/mol}, \Delta G^o = 29 \text{ KJ/mol} \qquad (4\text{-}32)$$

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H^o = -90.8 \text{ KJ/mol}, \Delta G^o = -25 \text{ KJ/mol} \qquad (4\text{-}34)$$

The operating temperature of this new method (523K) is in the same range as that of the conventional process (250-260^oC). This study was conducted at 3MPa pressure where as the conventional process operates at 5-8 MPa pressure. Thus, this potential process would operate at a pressure less than the conventional process. The selectivity to methanol in this study is comparable to that of the conventional process. Hence, this potentially new process is selected for HYSYS simulation (Indala, 2004). The block flow diagram is given in Figure 4.22 with stream definitions in Table 4-66.

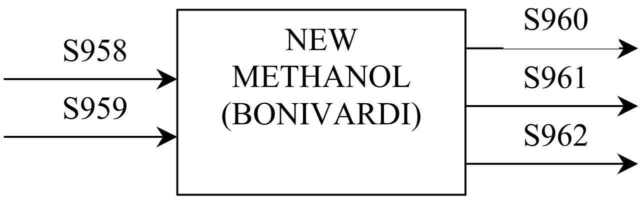


Figure 4.22 Block Diagram of New Methanol (Bonivardi) Process

Table 4-66 Description of Process Streams in New Methanol (Bonivardi) Process

Name of Streams	Description
Input Steams	
S958	CO_2 to new methanol (Bonivardi) process
S959	H_2 to new methanol (Bonivardi) process
Output Streams	
S960	CO produced from new methanol (Bonivardi) process
S961	Methanol produced from new methanol (Bonivardi) process
S962	Water produced from new methanol (Bonivardi) process

C-6-1-2. Material Balance and Energy Balance

Using the parameters in Table 4-67, the material balance and energy balance of new methanol (Bonivardi) process are given in Table 4-68.

In Table 4-68, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equations (4-32 and 4-33), the first equation is for the CO_2 balance; the second one is for the H_2 balance; the third one is for the H_2O balance; the last one is for the CO balance.

In the overall energy balance, Q_{NMEB} is heat input in the form of steam in heat exchanger and distillation column reboilers for heating reactants and product separation of the new methanol (Bonivardi) process, which is calculated from the energy balance. Q_{out} is the heat released removed by cooling water in heat exchanger and distillation column condensers for product separation in the new methanol

(Bonivardi) process based on the unit of methanol product, 9.2 MJ per lb of methanol (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

Table 4-67 Parameters in New Methanol (Bonivardi) Production, from Bonivardi, et al. (1998) and Indala (2004)

Name	Meaning	Value
COMe	Overall conversion of CO in new methanol (Bonivardi) process	0.9497
	Overall H_2 utilization in new methanol (Bonivardi) process	1

Table 4-68 Constraint Equations for New Methanol (Bonivardi) Production

Material Balance	
Overall	$(F_{958}+F_{959})-(F_{960}+F_{961}+F_{962})=0$
Species	CO_2: $\frac{F_{960}}{mw(CO)}+\frac{F_{961}}{mw(MeOH)}-\frac{F_{958}}{mw(CO_2)}=0$ H_2: $\frac{F_{960}}{mw(CO)}+\frac{3F_{961}}{mw(MeOH)}-\frac{F_{959}}{mw(H_2)}=0$ H_2O: $F_{962}-\frac{F_{958}(mw(H_2O))}{mw(CO_2)}=0$ CO: $F_{960}-\frac{F_{958}(mw(CO))(1-COMe)}{mw(CO_2)}=0$
Energy Balance	
Overall	$(F_{960}^{(CO)}/M^{(CO)}H_{960}^{(CO)}+F_{961}^{(MeOH)}/M^{(MeOH)}H_{961}^{(MeOH)}+F_{962}^{(H_2O)}/M^{(H_2O)}H_{962}^{(H_2O)})$ $-(F_{958}^{(CO_2)}/M^{(CO_2)}H_{958}^{(CO_2)}+F_{959}^{(H_2)}/M^{(H_2)}H_{959}^{(H_2)})+Q_{out}F_{961}^{(MeOH)}-Q_{NMEB}=0$
Enthalpy Function	$H_k^i(T)=(a_1^i+\frac{1}{2}a_2^iT+\frac{1}{3}a_3^iT^2+\frac{1}{4}a_4^iT^3+\frac{1}{5}a_5^iT^4+\frac{b_1^i}{T})RT$ J/mol $i = CO_2, H_2, CO, H_2O$ $k = 958, 959, 960, 962$ $H_k^{(MeOH)}(T)=(-238.54)(1000)+(79.225)(T-298.15)$ J/mol k=961 Source: Felder and Roussleu (1986)

In the material balance part, there are 5 variables and 5 equations including one dependent equation (overall material balance), so the number of degrees of freedom is

1. For the material and energy balance, there are 16 variables and 11 equations including the dependent overall material balance, so the number of degrees of freedom is 6.

C-6-2. New Methanol (Jun) Process (Jun, et al., 1998; Indala, 2004; Louisiana Chemical & Petroleum Products List, 1998)

C-6-2-1. Process Description

Jun, et al. (1998) described catalytic hydrogenation of CO_2 for the synthesis of methanol and dimethyl ether (DME) (oxygenates). The catalysts were hybrid catalyst of $Cu/ZnO/Cr_2O_3$ and CuNaY zeolite. The ratio of H_2 to CO_2 in the feed gas was 3:1. The reaction was carried out in a fixed bed micro-reactor at 523 K and 3MPa, and at a flow rate of 30 ml/min. The conversion of CO_2 to CO was 10.21% and to oxygenates was 9.37%. The selectivity of dimethyl ether in oxygenates was 36.7%. The reaction mechanism was provided as Equation (4-32, 4-34 and 4-69) (Jun, et al., 1998).

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta H^o = 41 \text{ KJ/mol}, \Delta G^o = 29 \text{ KJ/mol} \qquad (4\text{-}32)$$

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H^o = -90.8 \text{ KJ/mol}, \Delta G^o = -25 \text{ KJ/mol} \qquad (4\text{-}34)$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H^o = -24 \text{ KJ/mol}, \Delta G^o = -17 \text{ KJ/mol} \qquad (4\text{-}69)$$

The operating temperature of this new method (523K) is in the same range as that of the conventional process (250-260 ^oC). This study was conducted at 3MPa pressure where as the conventional process operates at 5-8 MPa pressure. Thus, this potential process would operate at a pressure less than the conventional process. DME is also produced as a by-product. Though the conversion of CO_2 to CO is less, through large recycle volumes, the total yield can be increased. Hence, this potentially new process was selected for HYSYS simulation (Indala, 2004).

The block flow diagram is given in Figure 4.23 with stream definitions from Table 4-69.

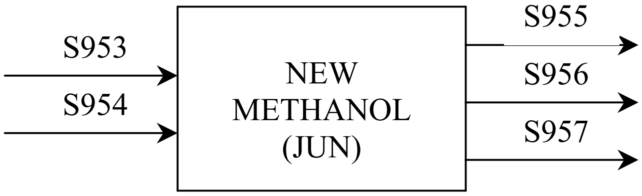


Figure 4.23 Block Diagram of New Methanol (Jun) Process

Table 4-69 Description of Process Streams in New Methanol (Jun) Process

Name of Streams	Description
Input Steams	
S953	CO_2 to new methanol (Jun) process
S954	H_2 to new methanol (Jun) process
Output Streams	
S955	Methanol produced from new methanol (Jun) process
S956	DME produced from new methanol (Jun) process
S957	Water produced from new methanol (Jun) process

C-6-2-2. Material Balance and Energy Balance

Using the parameters in Table 4-70, the material balance and energy balance of new methanol (Jun) process are given in Table 4-71.

Table 4-70 Parameters in New Methanol (Jun) Production, from Jun, et al. (1998) and Indala (2004)

Name	Meaning	Value
MeDME	Overall conversion of methanol to DME in new methanol (Jun) process	0.0519
	Overall CO_2 utilization in new methanol (Jun) process	1
	Overall H_2 utilization in new methanol (Jun) process	1

In Table 4-71, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equations (4-32, 4-34 and 4-69), the first equation is for the CO_2 balance; the second one is for the H_2 balance;

the third one is for the H_2O balance; the fourth one is for the DME balance; the last one is for the methanol balance.

Table 4-71 Constraint Equations for New Methanol (Jun) Production

Material Balance	
Overall	$(F_{953}+F_{954})-(F_{955}+F_{956}+F_{957})=0$
Species	CO_2: $F_{953}-(\frac{F_{955}}{mw(MeOH)}+\frac{F_{956}}{mw(DME)})mw(CO_2)=0$
	H_2: $F_{954}-(\frac{3F_{955}}{mw(MeOH)}+\frac{6F_{956}}{mw(DME)})mw(H_2)=0$
	H_2O: $(\frac{F_{953}}{mw(CO_2)}+\frac{F_{956}}{mw(DME)})mw(H_2O)-F_{957}=0$
	DME: $\frac{F_{953}(mw(DME))(MeDME)}{2mw(CO_2)}-F_{956}=0$
	MeOH: $\frac{F_{953}(mw(MeOH))(1-MeDME)}{mw(CO_2)}-F_{955}=0$
Energy Balance	
Overall	$(F_{955}^{(MeOH)}/M^{(MeOH)}H_{955}^{(MeOH)}+F_{956}^{(DME)}/M^{(DME)}H_{956}^{(DME)}+F_{957}^{(H_2O)}/M^{(H_2O)}H_{957}^{(H_2O)})-(F_{953}^{(CO_2)}/M^{(CO_2)}H_{953}^{(CO_2)}+F_{954}^{(H_2)}/M^{(H_2)}H_{954}^{(H_2)})+Q_{out}F_{955}^{(MeOH)}-Q_{NMEA}=0$
Enthalpy Function	$H_k^i(T)=(a_1^i+\frac{1}{2}a_2^iT+\frac{1}{3}a_3^iT^2+\frac{1}{4}a_4^iT^3+\frac{1}{5}a_5^iT^4+\frac{b_1^i}{T})RT$ J/mol i = CO_2, H_2, DME, H_2O k = 953, 954, 956, 957 $H_k^{(MeOH)}(T)=(-238.54)(1000)+(79.225)(T-298.15)$ J/mol k=955 Source: Felder and Roussleu (1986)

In the overall energy balance, Q_{NMEA} is heat input of the new methanol (Jun) process in the form of steam in heat exchanger and distillation column reboilers for heating reactants and product separation, which is calculated from the energy balance. Q_{out} is the heat released removed by cooling water in heat exchanger and distillation column condensers for product separation in the new methanol (Jun) process based on the unit of methanol product, 10.3 MJ per lb of methanol (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 5 variables and 6 equations including two dependent equations (overall material balance and CO_2 balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 16 variables and 12 equations including the dependent overall material balance and CO_2 balance, so the number of degrees of freedom is 6.

C-6-3. New Methanol (Nerlov) (Nerlov and Chorkendorff, 1999; Indala, 2004; Louisiana Chemical & Petroleum Products List, 1998)

C-6-3-1. Process Description

Nerlov and Chorkendorff (1999) described a laboratory scale process for the synthesis of methanol from CO_2 and H_2 over Cu(100) catalyst in a high-pressure cell at a temperature of 543 K and a pressure of 0.15 MPa. The average volume ratio of CO_2 to H_2 is about 2:3 in the feed gas. The rate of formation of methanol was 60 x 10^{-6} TurnOver Frequency (TOF) /site·s. The reaction mechanism (Equation 6-68) was provided without the CO_2 conversion rate.

$$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H^o = -49\ KJ/mol,\ \Delta G^o = 3\ KJ/mol \quad (4\text{-}68)$$

The operating temperature in this new method (543K) is in the same range as that of the conventional process (250-260 ^oC). The operating pressure in this method (0.15 MPa) is less than that of conventional process (5-8 MPa). Hence, this new methanol synthesis process was selected for HYSYS simulation (Indala, 2004).

The block flow diagram is given in Figure 4.24 with stream definitions from Table 4-72.

Figure 4.24 Block Diagram of New Methanol (Nerlov) Process

Table 4-72 Description of Process Streams in New Methanol (Nerlov) Process

Name of Streams	Description
Input Steams	
S963	CO_2 to new methanol (Nerlov) process
S964	H_2 to new methanol (Nerlov) process
Output Streams	
S965	Methanol produced from new methanol (Nerlov) process
S966	Water produced from new methanol (Nerlov) process

C-6-3-2. Material Balance and Energy Balance

Using the parameters in Table 4-73, the material balance and energy balance of new methanol (Nerlov) process are given in Table 4-74.

In Table 4-74, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equations (4-65), the first equation is for the CO_2 balance; the second one is for the H_2 balance; the last one is for the H_2O balance.

In the overall energy balance, Q_{NMEC} is heat input of the new methanol (Nerlov) process in the form of steam in heat exchanger and distillation column reboilers for heating reactants and product separation, which is calculated from the energy balance. Q_{out} is the heat ouput removed by cooling water in heat exchanger and distillation column condensers for cooling reactants and product separation in the new methanol (Nerlov) process based on the unit of methanol product, 12.6 MJ per lb of methanol (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 4 variables and 4 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 13 variables and 9 equations including the dependent overall material balance, so the number of degrees of freedom is 5.

Table 4-73 Parameters in New Methanol (Nerlov) Production, from Nerlov and Chorkendorff (1999) and Indala (2004)

Name	Meaning	Value
	Overall CO_2 utilization in new methanol (Jun) process	1
	Overall H_2 utilization in new methanol (Jun) process	1

Table 4-74 Constraint Equations for New Methanol (Nerlov) Production

Material Balance	
Overall	$(F_{963} + F_{964}) - (F_{965} + F_{966}) = 0$
Species	CO_2: $\frac{F_{963}}{mw(CO_2)} - \frac{F_{965}}{mw(MeOH)} = 0$ H_2: $\frac{F_{964}}{mw(H_2)} - \frac{3F_{965}}{mw(MeOH)} = 0$ H_2O: $\frac{F_{965}}{mw(MeOH)} - \frac{F_{966}}{mw(H_2O)} = 0$
Energy Balance	
Overall	$(F_{965}^{(MeOH)}/M^{(MeOH)}H_{965}^{(MeOH)} + F_{966}^{(H_2O)}/M^{(H_2O)}H_{966}^{(H_2O)})$ $- (F_{963}^{(CO_2)}/M^{(CO_2)}H_{963}^{(CO_2)} + F_{964}^{(H_2)}/M^{(H_2)}H_{964}^{(H_2)}) + Q_{out}F_{965}^{(MeOH)} - Q_{NMEC} = 0$
Enthalpy Function	$H_k^i(T) = (a_1^i + \frac{1}{2}a_2^iT + \frac{1}{3}a_3^iT^2 + \frac{1}{4}a_4^iT^3 + \frac{1}{5}a_5^iT^4 + \frac{b_1^i}{T})RT$ J/mol $i = CO_2, H_2, H_2O$ $k = 963, 964, 966$ $H_k^{(MeOH)}(T) = (-238.54)(1000) + (79.225)(T - 298.15)$ J/mol k=965 Source: Felder and Roussleu (1986)

C-6-4. New Methanol (Ushikoshi) (Ushikoshi, et al., 1998; Indala, 2004; Louisiana Chemical & Petroleum Products List, 1998)

C-6-4-1. Process Description

Ushikoshi, et al. (1998) described a pilot plant for methanol synthesis from CO_2 and H_2 with a production capacity of 50 kg/day over a multicomponent catalyst ($Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3$) under reaction condition of 523 K, 5 MPa and space velocity = 10000 h^{-1}. The ratio of H_2 to CO_2 in the feed gas was 3:1. The reaction mechanism was described as Equation (4-68, 4-32 and 4-34).

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad \Delta H^o = -49 \text{ KJ/mol}, \Delta G^o = 3 \text{ KJ/mol} \qquad (4\text{-}68)$$

$$CO_2 + H_2 \rightarrow CO + H_2O \quad \Delta H^o = 41 \text{ KJ/mol}, \Delta G^o = 29 \text{ KJ/mol} \qquad (4\text{-}32)$$

$$CO + 2H_2 \rightarrow CH_3OH \quad \Delta H^o = -90.8 \text{ KJ/mol}, \Delta G^o = -25 \text{ KJ/mol} \qquad (4\text{-}34)$$

Carbon dioxide and hydrogen supplied from gas cylinders were mixed and compressed along with recycled gases, and then fed into the reaction tube through a pre-heater (Ushikoshi, et al., 1998). The reaction products were cooled and the mixture of methanol and water was separated in a gas-liquid separator from unreacted gases and stored in a container ready for further separation (Ushikoshi, et al., 1998). The space-time yield of methanol was 700 g-CH_3OH/l-cat-h with the purity of 99.9% (Ushikoshi, et al., 1998). Since the conversion of CO_2 at 523 K and 5 MPa was 17%, the unreacted gases and gaseous products like CO were recycled back to the reactor (Ushikoshi, et al., 1998).

Ushikoshi, et al. (1998) compared the new catalyst ($Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3$) performance with a commercial $Cu/ZnO/Al_2O_3$ catalyst and concluded that the new catalyst exhibited a higher activity of over 700 g-

CH_3OH/l-cat-h whereas the commercial catalyst exhibited an activity of 550 g-CH_3OH/l-cat-h. But they did not report an exact time period for catalyst deactivation. On the other hand, the operating temperature and pressure of the new process (523K and 5 MPa) were in the same range as that of the conventional process (250-260^{o}C and 5MPa). The purity of methanol produced was 99.9%. Hence, this potentially new process was selected for HYSYS simulation (Indala, 2004).

The block flow diagram is given in Figure 4.25 with stream definitions from Table 4-75.

Figure 4.25 Block Diagram of New Methanol (Ushikoshi) Process

Table 4-75 Description of Process Streams in New Methanol (Ushikoshi) Process

Name of Streams	Description
Input Steams	
S967	CO_2 to new methanol (Ushikoshi) process
S968	H_2 to new methanol (Ushikoshi) process
Output Streams	
S969	Methanol produced from new methanol (Ushikoshi) process
S970	Water produced from new methanol (Ushikoshi) process
S990	CO produced from new methanol (Ushikoshi) process

C-6-4-2. Material Balance and Energy Balance

Using the parameters in Table 4-76, the material balance and energy balance of new methanol (Ushikoshi) process are given in Table 4-77.

In Table 4-77, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equations (4-32, 4-34 and 4-68), the first equation is for the CO_2 balance; the second one is for the H_2 balance; the third one is for the H_2O balance; the last one is for the CO balance.

Table 4-76 Parameters in New Methanol (Ushikoshi) Production, from Ushikoshi, et al. (1998) and Indala (2004)

Name	Meaning	Value
CIDMe	CO_2 indirect conversion to CO in new methanol (Ushikoshi) process	0.1176
CODCMe	CO conversion to methanol in new methanol (Ushikoshi) process	0.90
	Overall H_2 utilization in new methanol (Ushikoshi) process	1
	Overall CO_2 utilization in new methanol (Ushikoshi) process	1

Table 4-77 Constraint Equations for New Methanol (Ushikoshi) Production

Material Balance	
Overall	$(F_{967} + F_{968}) - (F_{969} + F_{970} + F_{990}) = 0$
Species	CO_2: $F_{967} - (\frac{F_{969}}{mw(MeOH)} + \frac{F_{990}}{mw(CO)})mw(CO_2) = 0$
	H_2: $F_{968} - (\frac{3F_{969}}{mw(MeOH)} + \frac{F_{990}}{mw(CO)})mw(H_2) = 0$
	H_2O: $(\frac{F_{969}}{mw(MeOH)} + \frac{F_{990}}{mw(CO)})mw(H_2O) - F_{970} = 0$
	CO: $\frac{F_{967}(mw(CO))(CIDMe)(1 - CODCMe)}{mw(CO_2)} - F_{990} = 0$
Energy Balance	
Overall	$(F_{969}^{(MeOH)} / M^{(MeOH)} H_{969}^{(MeOH)} + F_{970}^{(H_2O)} / M^{(H_2O)} H_{970}^{(H_2O)} + F_{990}^{(CO)} / M^{(CO)} H_{990}^{(CO)})$
	$- (F_{967}^{(CO_2)} / M^{(CO_2)} H_{967}^{(CO_2)} + F_{968}^{(H_2)} / M^{(H_2)} H_{968}^{(H_2)}) + Q_{out} F_{969}^{(MeOH)} - Q_{NMED} = 0$
Enthalpy Function	$H_k^i(T) = (a_1^i + \frac{1}{2}a_2^i T + \frac{1}{3}a_3^i T^2 + \frac{1}{4}a_4^i T^3 + \frac{1}{5}a_5^i T^4 + \frac{b_1^i}{T})RT$ J/mol
	i = CO_2, H_2, H_2O, CO; k = 967, 968, 970, 990
	$H_k^{(MeOH)}(T) = (-238.54)(1000) + (79.225)(T - 298.15)$ J/mol k=969
	Source: Felder and Roussleu (1986)

In the overall energy balance, Q_{NMED} is heat input of the new methanol (Ushikoshi) process in the form of steam in heat exchanger and distillation column reboilers for heating reactants and product separation, which is calculated from the energy balance. Q_{out} is the heat ouput removed by cooling water in heat exchanger and distillation column condensers for cooling reactants and product separation in the new methanol (Ushikoshi) process based on the unit of methanol product, 11.5 MJ per lb of methanol (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 5 variables and 5 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 16 variables and 11 equations including the dependent overall material balance, so the number of degrees of freedom is 6.

C-7. Formic Acid (New Process) (Wells, 1999; Thomas, et al., 2001; Dinjus, 1998; Indala, 2004)

Currently, there are four commercial formic acid processes: hydrolysis of formamide; hydrolysis of methyl formate; acidolysis of formate salts; and oxidation of n-butane or naphtha where it is a by-product. Over half of formic acid production worldwide comes from hydrolysis of methyl formate because of the lower raw material cost (Wells, 1999). The formation of by-product ammonium sulfate made hydrolysis of formamide unattractive. The production as a by-product from oxidation of n-butane and naphtha to acetic acid has declined due to the commercial acetic acid process without the formic acid by-product.

Wells (1999) gave a brief description of the production of formic acid by hydrolysis of methyl formate. Methanol is reacted with dilute or impure anhydrous CO in the liquid phase at 80ºC and 4.5 MPa over sodium methoxide catalyst with 2.5% concentration. Methyl formate is the reaction product and unreacted CO is recycled with the conversion of 64% per pass (Equation 4-70). Methyl formate is degassed and hydrolyzed with excess water to overcome the unfavorable equilibrium constant at 80ºC and under increased pressure (Equation 4-71). The reactor effluent contains unreacted water and methyl formate, and produced formic acid and methanol. Methanol and methyl formate are recovered overhead and recycled. The remaining formic acid-water mixture is distilled and excess water is removed in an extraction tower using secondary amide to extract. The product obtained is a 90% solution of formic acid

$$CH_3OH + CO \rightarrow HCOOCH_3 \qquad \Delta H^o = -46 \text{ KJ/mol}, \Delta G^o = 2 \text{ KJ/mol} \quad (4\text{-}70)$$

$$HCOOCH_3 + H_2O \rightarrow HCOOH + CH_3OH \qquad \Delta H^o = 20 \text{ KJ/mol}, \Delta G^o = 13 \text{ KJ/mol} \quad (4\text{-}71)$$

Compared to the conventional formic acid process, there are two potentially new processes that use carbon dioxide for the production of formic acid. Thomas, et al. (2001) described a laboratory process for the synthesis of formic acid through CO_2 hydrogenation in liquid triethylamine over $RuCl(O_2CMe)(PMe_3)_4$ catalyst at 50°C and 10MPa (Equation 4-72). The volume ratio of H_2 to CO_2 was 2:3. However, no separation techniques for the formic acid-triethylamine mixture were provided, and conversion of the reactants in the reaction was also not mentioned. The new process described by Dinjus (1998) will be discussed in detail in the next section.

$$CO_2 + H_2 + ½\ N(C_2H_5)_3 \rightarrow ½\ [HCOOH]_2N(C_2H_5)_3 \quad (4\text{-}72)$$

Since a production capacity of formic acid was not available in Louisiana Chemical & Petroleum Products List (1998) and Wells (1999) gave the typical production capacities of formic acid ranged from 6,000 to 150,000 metric tons per year. Hence, an average of production capacity of 78,000 metric tons per year was used for this potentially new process.

C-7-1. Process Description

Dinjus (1998) described an experimental study for the production of formic acid through hydrogenation of carbon dioxide in aqueous solution over Wilkinson's catalyst [ClRh(TPPTS)$_3$] at 25°C and 4 MPa (Equation 4-73). The synthesis rate of formic acid was 3,440 mol formic acid per mol of catalyst. This new method (25°C and 4MPa) has mild reaction condition than the conventional one (50°C and 4.5 MPa). On the other hand, the purification costs for the raw material CO_2 can be eliminated due to the aqueous solution reaction media since industrial CO_2 removal from process waste streams is predominantly carried out in water (Dinjus, 1998). Hence, this new potential process is selected for HYSYS simulation (Indala, 2004). The block flow diagram is given in Figure 4.26 with stream definitions from Table 4-78.

$$CO_2\ (g) + H_2\ (g) \rightarrow HCOOH\ (l) \qquad \Delta H^o = -31\ KJ/mol,\ \Delta G^o = 33\ KJ/mol \quad (4\text{-}73)$$

Figure 4.26 Block Diagram of New Formic Acid Process

Table 4-78 Description of Process Streams in New Formic Acid Process

Name of Streams	Description
Input Steams	
S942	CO_2 to new formic acid process
S943	H_2 to new formic acid process
Output Streams	
S944	Formic acid produced from new formic acid process

C-7-2. Material Balance and Energy Balance

Using the parameters in Table 4-79, the material balance and energy balance of new formic acid process are given in Table 4-80.

In Table 4-80, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equations (4-73), the first equation is for the HCOOH balance; the second one is for the CO_2 balance.

In the overall energy balance, Q_{FA} is heat input of the new formic acid process in the form of steam in heat exchanger and distillation column reboilers for heating reactants and product separation, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in heat exchanger and distillation column condensers for cooling reactants and product separation in the new formic acid process based on the unit of methanol product, 389 KJ per lb of formic acid (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 3 variables and 3 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 10 variables and 7 equations including the dependent overall material balance, so the number of degrees of freedom is 4.

Table 4-79 Parameters in New Formic Acid Production, from Dinjus (1998) and Indala (2004)

Name	Meaning	Value
	Overall H_2 utilization in new formic acid process	1
	Overall CO_2 utilization in new formic acid process	1

Table 4-80 Constraint Equations for New Formic Acid Production

Material Balance	
Overall	$(F_{942} + F_{943}) - F_{944} = 0$
Species	HCOOH: $\frac{F_{943}}{mw(H_2)} mw(HCOOH) - F_{944} = 0$
	CO_2: $F_{942} - \frac{F_{943}}{mw(H_2)} mw(CO_2) = 0$
Energy Balance	
Overall	$F_{944}^{(HCOOH)} / M^{(HCOOH)} H_{944}^{(HCOOH)} - (F_{942}^{(CO_2)} / M^{(CO_2)} H_{942}^{(CO_2)} + F_{943}^{(H_2)} / M^{(H_2)} H_{943}^{(H_2)})$
	$+ Q_{out} F_{944}^{(HCOOH)} - Q_{FA} = 0$
Enthalpy Function	$H_k^i(T) = (a_1^i + \frac{1}{2} a_2^i T + \frac{1}{3} a_3^i T^2 + \frac{1}{4} a_4^i T^3 + \frac{1}{5} a_5^i T^4 + \frac{b_1^i}{T}) RT$ J/mol
	$i = CO_2, H_2$
	$k = 942, 943$
	$H_k^{(HCOOH)}(T) = (-424.7)(1000) + (99.5)(T - 298.15)$ J/mol k=944
	Source: Knovel (2003)

C-8. Methylamines (New Process) (Wells, 1999; Arakawa, 1998; Indala, 2004)

Currently, all three methylamines (mono-, di-, and tri-methylamine, i.e., MMA, DMA, TMA) are produced by catalytic alkylation of anhydrous ammonia with methanol. It is not economic to produce only one of the amines even though DMA is the most desired isomer (Wells, 1999). Another process for methylamines production uses formaldehyde instead of methanol. The choice of route is determined by the cost of raw materials (Wells, 1999).

In the conventional process that uses methanol, vaporized methanol and ammonia with a molar ratio of 1:2 react at 390-450°C and 1.4 MPa over amorphous silica-aluminum oxides as catalyst (Equation 4-74, 4-75 and 4-76). The unreacted methanol and ammonia are separated and recycled back. The methylamine mixture is extractively distilled under pressure with water. Because the market demand is mainly for MMA and DMA, most of the formed TMA is recycled back. A total yield of 95% is obtained in this process (Wells, 1999).

$$CH_3OH + NH_3 \rightarrow CH_3NH_2 + H_2O \qquad \Delta H^o = -17\ KJ/mol,\ \Delta G^o = -17\ KJ/mol \quad (4\text{-}74)$$

$$CH_3OH + CH_3NH_2 \rightarrow (CH_3)_2NH + H_2O \quad \Delta H^o = -37\ KJ/mol,\ \Delta G^o = -30\ KJ/mol \quad (4\text{-}75)$$

$$CH_3OH + (CH_3)_2NH \rightarrow (CH_3)_3N + H_2O \quad \Delta H^o = -46\ KJ/mol,\ \Delta G^o = -36\ KJ/mol \quad (4\text{-}76)$$

A potentially new process that uses CO_2 for methylamines production is given by Arakawa (1998). This potential process selected for HYSYS simulation is discussed in detail in the next section (Indala, 2004).

Since a production capacity of methylamines was not available in Louisiana Chemical & Petroleum Products List (1998) and Wells (1999) gave the typical production capacities of methylamines ranged from 10,000 to 100,000 metric tons per year. Hence, an average of production capacity of 55,000 metric tons per year was used as a basis. The production capacity for MMA of this process was set to be 26,400 metric tons per year.

C-8-1. Process Description

Arakawa (1998) described an experimental process for the production of methylamines from a mixture of CO_2, H_2, and NH_3 over Cu/Al_2O_3 catalyst at 277°C and 0.6 MPa with feed gas composition $H_2/CO_2/NH_3 = 3/1/1$ (Equation 4-32, 4-34, 4-74 and 4-75). MMA and DMA were produced effectively with by-product CO (Arakawa, 1998). Because this new experimental process (277°C and 0.6MPa) operates at a lesser temperature and pressure than the conventional process (390-450°C and 1.4MPa), it is competitive with the conventional process.

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta H^o = 41 \text{ KJ/mol}, \Delta G^o = 29 \text{ KJ/mol} \quad (4\text{-}32)$$

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H^o = -90.5 \text{ KJ/mol}, \Delta G^o = -25 \text{ KJ/mol} \quad (4\text{-}34)$$

$$CH_3OH + NH_3 \rightarrow CH_3NH_2 + H_2O \qquad \Delta H^o = -17 \text{ KJ/mol}, \Delta G^o = -17 \text{ KJ/mol} \quad (4\text{-}74)$$

$$CH_3OH + CH_3NH_2 \rightarrow (CH_3)_2NH + H_2O \qquad \Delta H^o = -37 \text{ KJ/mol}, \Delta G^o = -30 \text{ KJ/mol} \quad (4\text{-}75)$$

The block flow diagram is given in Figure 4.27 with stream definitions from Table 4-81.

Figure 4.27 Block Diagram of New Methylamines Process

C-8-2. Material Balance and Energy Balance

Using the parameters in Table 4-82, the material balance and energy balance of new methylamines process are given in Table 4-83.

Table 4-81 Description of Process Streams in New Methylamines Process

Name of Streams	Description
Input Steams	
S946	CO_2 to new methylamines process
S947	H_2 to new methylamines process
S948	NH_3 to new methylamines process
Output Streams	
S949	CO and CO_2 mixture gas produced from new methylamines process
S950	MMA produced from new methylamines process
S951	DMA produced from new methylamines process
S952	Water produced from new methylamines process

Table 4-82 Parameters in New Methylamines Production, from Arakawa (1998) and Indala (2004)

Name	Meaning	Value
CDCONV	CO_2 conversion in new methylamines process	0.9978
COCONV	CO conversion in new methylamines process	0.90
MMASE	MMA final selectivity based on methanol in new methylamines process	0.40
DMASE	DMA final selectivity based on methanol in new methylamines process	0.60
	Methanol conversion in new methylamines process	1

In Table 4-83, the overall material balance for the whole process is given with the mixture stream expression. For the species material balance obtained using the reaction equations (4-32, 4-34, 4-74 and 4-75), the first equation is for the CO_2 balance; the second one is for the H_2 balance; the third one is for the NH_3 balance; the fourth one is for the CO balance; the fifth one is for the MMA balance; the sixth one is for the DMA balance; the last one is for the water balance.

In the overall energy balance, Q_{MA} is heat input of the new methylamines process in the form of steam in heat exchanger and distillation column reboilers for heating reactants and product separation, which is calculated from the energy balance.

Table 4-83 Constraint Equations for New Methylamines Production

Material Balance	
Overall	$(F_{946}+F_{947}+F_{948})-(F_{949}+F_{950}+F_{951}+F_{952})=0$ $F_{949}=F_{949}^{(CO)}+F_{949}^{(CO_2)}$
Species	CO_2: $F_{946}-(F_{949}^{(CO_2)}+F_{946}(CDCONV))=0$ H_2: $F_{947}-(\frac{3F_{950}}{mw(MMA)}+\frac{6F_{951}}{mw(DMA)}+\frac{F_{949}^{(CO)}}{mw(CO)})mw(H_2)=0$ NH_3: $F_{948}-(\frac{F_{950}}{mw(MMA)}+\frac{F_{951}}{mw(DMA)})mw(NH_3)=0$ CO: $\frac{F_{946}(mw(CO))(CDCONV)(1-COCONV)}{mw(CO_2)}-F_{949}^{(CO)}=0$ MMA: $\frac{F_{946}(mw(MMA))(CDCONV)(COCONV)(MMASE)}{mw(CO_2)}-F_{950}=0$ DMA: $\frac{F_{946}(mw(DMA))(CDCONV)(COCONV)(DMASE)}{(2)mw(CO_2)}-F_{951}=0$ H_2O: $(\frac{F_{946}(CDCONV)}{mw(CO_2)}+\frac{F_{950}}{mw(MMA)}+\frac{2F_{951}}{mw(DMA)})mw(H_2O)-F_{952}=0$
Energy Balance	
Overall	$(\Sigma F_{949}^{(i)}/M^{(i)}H_{949}^{(i)}+F_{950}^{(MMA)}/M^{(MMA)}H_{950}^{(MMA)}+F_{951}^{(DMA)}/M^{(DMA)}H_{951}^{(DMA)}$ $+F_{952}^{(H_2O)}/M^{(H_2O)}H_{952}^{(H_2O)})-(F_{946}^{(CO_2)}/M^{(CO_2)}H_{946}^{(CO_2)}+F_{947}^{(H_2)}/M^{(H_2)}H_{947}^{(H_2)}$ $+F_{948}^{(NH_3)}/M^{(NH_3)}H_{948}^{(NH_3)})+Q_{out}(F_{950}^{(MMA)}+F_{951}^{(DMA)})-Q_{MA}=0$ where i = CO, CO_2
Enthalpy Function	$H_k^i(T)=(a_1^i+\frac{1}{2}a_2^iT+\frac{1}{3}a_3^iT^2+\frac{1}{4}a_4^iT^3+\frac{1}{5}a_5^iT^4+\frac{b_1^i}{T})RT$ J/mol i = CO_2, H_2, NH_3, CO, H_2O k = 946, 947, 948, 949, 952 $H_k^{(MMA)}(T)=(-22.5)(1000)+(50.1)(T-298.15)$ J/mol k=950 Source: Knovel (2003) $H_k^{(DMA)}(T)=(-18.5)(1000)+(70.7)(T-298.15)$ J/mol k=951 Source: Knovel (2003)

Q_{out} is the heat ouput removed by cooling water in heat exchanger and distillation column condensers for cooling reactants and product separation in the new methylamines process based on the unit of methylamines product, 11.7 MJ per lb of methylamines (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 9 variables and 9 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 25 variables and 18 equations including the dependent overall material balance, so the number of degrees of freedom is 8.

C-9. Ethanol (EtOH) (New Process) (Wells, 1999; Speight, 2002; Inui, 2002; Kusama, et al., 1998; Bando, et al., 1998; Yamamoto and Inui, 1998; Takagawa, et al., 1998; Izumi, et al., 1998; Higuchi, et al., 1998; Indala, 2004; Louisiana Chemical & Petroleum Products List, 1998)

There are three commercial processes for ethanol production (Wells, 1999). The first one is the indirect catalytic hydration of ethylene with disadvantages such as handling large volumes of dilute sulfuric acid, energy required for its concentration, and corrosion caused by the acid. The second one is direct catalytic hydration of ethylene over phosphoric acid absorbed onto silica gel catalyst at 230-300°C and 6-8 MPa (Equation 4-77). The molar ratio of ethylene to water is 1:0.3-0.8 (Wells, 1999). The conversion of ethylene to ethanol is about 4% per pass with a net yield of 97% due to large recycle volume of unconverted ethylene and diethyl ether (Equation 4-78) (Speight, 2002). The third new process for ethanol synthesis has three steps: carbonylation of methanol with carbon monoxide to acetic acid; acetic acid esterified with methanol to methyl acetate; and methyl acetate hydrogenolysis to ethanol and methanol. Wells (1999) gave the overall reaction equation (4-79).

$CH_2 = CH_2 + H_2O \rightarrow C_2H_5OH$ $\Delta H^o = -45.5$ KJ/mol, $\Delta G^o = -8$ KJ/mol (4-77)

$2C_2H_5OH \leftrightarrow (C_2H_5)_2O + H_2O$ $\Delta H^o = -24$ KJ/mol, $\Delta G^o = -15$ KJ/mol (4-78)

$CH_3OH + CO + 2H_2 \rightarrow C_2H_5OH + H_2O$ $\Delta H^o = -165$ KJ/mol, $\Delta G^o = -97$ KJ/mol (4-79)

For potentially new processes for ethanol from carbon dioxide, Inui (2002) reviewed five experimental processes for synthesis of ethyl alcohol from the hydrogenation of carbon dioxide with the same ratio of H_2 to CO_2 = 3:1 (Equation 4-80). In the first case, the reaction condition was 573 K and 6.9 MPa over Rh-Li-Fe/SiO_2 catalyst with 10.5% both of the conversion of carbon dioxide to ethanol and the selectivity to ethanol. In the second case, the reaction condition was 513-533K and 4.9 MPa over Cu-Zn-Fe-K catalyst with 21.2% both of the conversion of carbon dioxide to ethanol and the selectivity to ethanol. In the third case, the reaction condition was 583 K and 8 MPa over Fe-Cu-Zn-Al-K catalyst with 28.5% both of the conversion of carbon dioxide and the selectivity to ethanol. In the fourth case, the reaction condition was 623 K and 8 MPa over (Rh/MFI-silicate)-(Fe-Cu-Zn-Al-K) catalyst with 12.8% both of the conversion of carbon dioxide and the selectivity to ethanol. In the fifth case, the reaction condition was 603 K and 8 MPa over (Fe-Cu-Al-K)-(Cu-Zn-Al-K.Ga.Pd) catalyst with 25.1% both of the conversion of carbon dioxide and the selectivity to ethanol.

$2CO_2 + 6H_2 \rightarrow C_2H_5OH + 3H_2O$ $\Delta H^o = -173$ KJ/mol, $\Delta G^o = -65$ KJ/mol (4-80)

Kusama, et al. (1998) described a laboratory process for ethanol synthesis through hydrogenation of carbon dioxide over Rh/SiO_2 catalyst at 533K and 5 MPa with the feed gas composition H_2:CO_2 = 3:1 and 2% of the selectivity to ethanol (Equation 4-80).

Bando, et al. (1998) gave an experimental process for the hydrogenation of carbon dioxide over Rh ion exchanged zeolite catalysts at 523 K and 3 MPa with the feed gas contains hydrogen and carbon dioxide with a composition of 3:1, along with 1.8% CO. No reaction mechanism was provided. Main products were methane, carbon monoxide, and ethyl alcohol with 7% of conversion of carbon dioxide and 16%, 40%, 38% of selectivity to ethanol, methane and carbon monoxide, respectively.

Yamamoto and Inui (1998) provided a method for the synthesis of ethanol over Cu-Zn-Al-K and Fe-Cu-Al-K mixed oxide catalyst at 603K and 8 MPa with the feed gas composition H_2/CO_2 = 3/1. No reaction mechanism was provided. The products were ethyl alcohol, methanol, hydrocarbons, and carbon monoxide. The CO_2 overall conversion was 54.5% with 5% to ethanol.

Takagawa, et al. (1998) described hydrogenation of carbon dioxide for the synthesis of ethanol over K/Cu-Zn-Fe oxide catalyst at 573K and 7MPa with 3:1of the ratio of H_2 to CO_2. CO_2 conversion was 44% and selectivity to ethanol was 20%.

Izumi, et al. (1998) gave an experimental process for ethanol from carbon dioxide and hydrogen over $[Rh_{10}Se]/TiO_2$ catalyst at 623K and 47 kPa with the ratio of 2:1 H_2 to CO_2. The reaction path for the formation of ethanol was described as CH_x (a) + CO_y (a) → acetate (a) → ethanol. CO_2 conversion was 83% and ethanol selectivity was 80%.

In general, the above potentially new processes for ethanol synthesis from CO_2 and hydrogen are not as profitable as the new process described by Higuchi, et al. (1998) which is discussed in detail in the next section (Indala, 2004).

The capacity of this process is set to be 104,000 metric tons per year of ethanol. This was based on an ethanol plant of Shepherd Oil, located in Jennings, LA, with the capacity of 300 million gallons of ethanol per year (108,000 metric tons per year) (Louisiana Chemical & Petroleum Products List, 1998).

C-9-1. Process Description

Higuchi, et al. (1998) described an experimental process for the ethanol synthesis from CO_2 hydrogenation over K/Cu-Zn-Fe-Cr oxide catalyst in a conventional flow reactor at 300°C and 7 MPa (Equation 4-80). The catalyst exhibited a long catalytic life because of its slow segregation rate. The conversion rate of CO_2 was 35% and selectivity to ethanol was 16%.

$$2CO_2 + 6H_2 \rightarrow C_2H_5OH + 3H_2O \qquad \Delta H^o = -173 \text{ KJ/mol}, \Delta G^o = -65 \text{ KJ/mol} \quad (4\text{-}80)$$

Compared with the conventional process, the operating temperature and pressure of the new process (300°C and 7 MPa) are in the same range as those of conventional process (230-300°C and 6-8 MPa). The 35% conversion of CO_2 is higher than the 4% conversion of ethylene to ethanol per pass in conventional process. Meanwhile, the catalyst used in the new process had a long life without deactivation. Hence, this new process was selected for HYSYS simulation and incorporated into the chemical complex.

The block flow diagram is given in Figure 4.28 with stream definitions from Table 4-84.

Figure 4.28 Block Diagram of New Ethanol Process

Table 4-84 Description of Process Streams in New Ethanol Process

Name of Streams	Description
Input Steams	
S980	CO_2 to new ethanol process
S981	H_2 to new ethanol process
Output Streams	
S982	Ethanol solution produced from new ethanol process
S983	Water produced from new ethanol process

C-9-2. Material Balance and Energy Balance

Using the parameters in Table 4-85, the material balance and energy balance of new ethanol process are given in Table 4-86.

Table 4-85 Parameters in New Ethanol Production, from Higuchi, et al. (1998) and Indala (2004)

Name	Meaning	Value
WTEtB	Weight fraction of ethanol solute in ethanol solution in new ethanol process	0.88
	Overall CO_2 utilization in new ethanol process	1
	Overall H_2 utilization in new ethanol process	1

In Table 4-86, the overall material balance for the whole process is given with the mixture stream expression. For the species material balance obtained using the reaction equations (4-80), the first equation is for the CO_2 balance; the second one is for the H_2 balance; the last one is for the water balance.

Table 4-86 Constraint Equations for New Ethanol Production

Material Balance	
Overall	$(F_{980}+F_{981})-(F_{982}+F_{983})=0$
	$F_{982}=F_{982}^{(EtOH)}+F_{982}^{(H_2O)}$
Species	CO_2: $F_{980}-\dfrac{2F_{982}^{(EtOH)}}{mw(EtOH)}mw(CO_2)=0$
	H_2: $F_{981}-\dfrac{6F_{982}^{(EtOH)}}{mw(EtOH)}mw(H_2)=0$
	H_2O: $\dfrac{3F_{982}^{(EtOH)}}{mw(EtOH)}mw(H_2O)-(F_{983}+F_{982}^{(H_2O)})=0$
Energy Balance	
Overall	$(\Sigma F_{982}^{(i)}/M^{(i)}H_{982}^{(i)}+F_{983}^{(H_2O)}/M^{(H_2O)}H_{983}^{(H_2O)})-(F_{980}^{(CO_2)}/M^{(CO_2)}H_{980}^{(CO_2)}$
	$+F_{981}^{(H_2)}/M^{(H_2)}H_{981}^{(H_2)})+Q_{out}F_{982}-Q_{ETB}=0$
	where i = EtOH, H_2O
Enthalpy Function	$H_k^i(T)=(a_1^i+\frac{1}{2}a_2^iT+\frac{1}{3}a_3^iT^2+\frac{1}{4}a_4^iT^3+\frac{1}{5}a_5^iT^4+\frac{b_1^i}{T})RT$ J/mol
	i = CO_2, H_2, H_2O
	k = 980, 981, 982, 983
	$H_k^{(EtOH)}(T)=(-277.6)(1000)+(112.3)(T-298.15)$ J/mol k=982
	Source: Knovel (2003)

In the overall energy balance, Q_{ETB} is heat input of the new ethanol process in the form of steam in heat exchanger and distillation column reboilers for heating reactants and product separation, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in heat exchanger and distillation column condensers for cooling reactants and product separation in the new ethanol process based on the unit of ethanol solution product, 13.5 MJ per lb of ethanol solution (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 6 variables and 6 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 16 variables and 12 equations including the dependent overall material balance, so the number of degrees of freedom is 5.

C-10. Dimethyl Ether (DME) (New process) (Turton, et al., 1998; Tao, et al., 2001; Jun, et al., 1998; Romani, et al., 2000; Jun, et al., 2002; Indala, 2004)

Dimethyl ether (DME) is produced commercially by catalytic dehydration of methanol over an amorphous alumina catalyst treated with 10.2% silica at 250-368ºC and 1.5 MPa (Equation 4-69) (Turton, et al., 1998). The single-pass conversion of methanol is about 80%.

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H^o = -24 \text{ KJ/mol}, \Delta G^o = -17 \text{ KJ/mol} \quad (4\text{-}69)$$

There are four new experimental studies for the production of DME where three use CO_2 as a raw material and the other one uses natural gas as a feedstock. These are described below.

Tao, et al. (2001) reported a laboratory process for the production of methanol and DME from CO_2 hydrogenation over the mixture catalysts of Cu-Zn-Al-Cr mixed oxide catalyst and HZSM catalyst ($Cu\text{-}ZnO\text{-}Al_2O_3\text{-}Cr_2O_3$ + H-ZSM-5 ($SiO_2/Al_2O_3=80$)) at 523 K and 3 MPa (Equation 4-68 and 4-69). The total yield of DME and methanol was higher than 26% with over 90% selectivity to DME.

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H^o = - 49 \text{ KJ/mol}, \Delta G^o = 3.5 \text{ KJ/mol} \quad (4\text{-}68)$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H^o = -24 \text{ KJ/mol}, \Delta G^o = -17 \text{ KJ/mol} \quad (4\text{-}69)$$

Jun, et al. (1998) described a process for production of methanol and DME by CO_2 hydrogenation over a hybrid catalyst of Cu/ZnO/Cr_2O_3 and CuNaY zeolite, which was discussed in the new methanol production section.

Romani, et al. (2000) described a three-step large-scale process for the production of DME from natural gas, synthesis gas preparation, synthesis of methanol and DME, and product separation and purification. Since the research interest is the processes consume CO_2, this process is not considered.

Above three processes are not included in the chemical complex because they were not competitive with the potentially new process described by Jun, et al. (2002) which is discussed in detail in the following section.

Since there was no available production capacity for DME in Louisiana Chemical & Petroleum Products List (1998), a typical production capacity of 100 million pounds per year was taken as a basis. Hence, the capacity of the new process for DME was set to be 45,800 metric tons per year (Indala, 2004).

C-10-1. Process Description

Jun, et al. (2002) gave a potentially new process for the synthesis of DME from CO_2 hydrogenation over the γ-Al_2O_3 modified with 1% silica catalyst in a fixed-bed reactor at 523 K and 0.053 MPa (Equation 4-32, 4-34 and 4-69). The conversion of intermediate methanol to DME was 70%.

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta H^o = 41 \text{ KJ/mol}, \Delta G^o = 29 \text{ KJ/mol} \qquad (4\text{-}32)$$

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H^o = -90.8 \text{ KJ/mol}, \Delta G^o = -25 \text{ KJ/mol} \qquad (4\text{-}34)$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \quad \Delta H^o = -24 \text{ KJ/mol}, \Delta G^o = -17 \text{ KJ/mol} \qquad (4\text{-}69)$$

Compared to the conventional process, the operating condition of the new process (523 K and 0.053 MPa) is milder than that of the conventional process (523-641 K and 1.5 MPa). The intermediate methanol conversion to DME in the new process is 70% closer to the 80% conversion in the conventional process.

The block flow diagram is given in Figure 4.29 with stream definitions from Table 4-87.

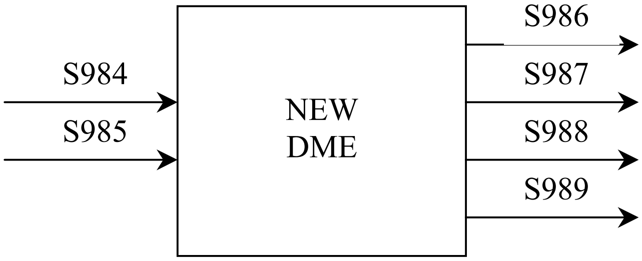


Figure 4.29 Block Diagram of New DME Process

Table 4-87 Description of Process Streams in New DME Process

Name of Streams	Description
Input Steams	
S984	CO_2 to new DME process
S985	H_2 to new DME process
Output Streams	
S986	CO produced from new DME process
S987	DME produced from new DME process
S988	Methanol produced from new DME process
S989	Water produced from new DME process

C-10-2. Material Balance and Energy Balance

Using the parameters in Table 4-88, the material balance and energy balance of new DME process are given in Table 4-89.

In Table 4-89, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equations (4-32, 4-34 and

Table 4-88 Parameters in New DME Production, from Jun, et al. (2002) and Indala (2004)

Name	Meaning	Value
COMeD	CO conversion rate to methanol in new DME process	0.63
MeDMED	Methanol conversion rate to DME in new DME process	0.89
	Overall CO_2 conversion rate in new DME process	1

Table 4-89 Constraint Equations for New DME Production

Material Balance

Overall

$$(F_{984}+F_{985})-(F_{986}+F_{987}+F_{988}+F_{989})=0$$

Species

$$CO_2\text{:}\ F_{984}-(\frac{F_{986}}{mw(CO)}+\frac{2F_{987}}{mw(DME)}+\frac{F_{988}}{mw(MeOH)})mw(CO_2)=0$$

$$H_2\text{:}\ F_{985}-(\frac{F_{986}}{mw(CO)}+\frac{6F_{987}}{mw(DME)}+\frac{3F_{988}}{mw(MeOH)})mw(H_2)=0$$

$$CO\text{:}\ \frac{F_{984}(1-COMeD)}{mw(CO_2)}mw(CO)-F_{986}=0$$

$$DME\text{:}\ \frac{F_{984}(COMeD)(MeDME)}{(2)mw(CO_2)}mw(DME)-F_{987}=0$$

$$MeOH\text{:}\ \frac{F_{984}(COMeD)(1-MeDMED)}{mw(CO_2)}mw(MeOH)-F_{988}=0$$

$$H_2O\text{:}\ (\frac{F_{984}}{mw(CO_2)}+\frac{F_{987}}{mw(DME)})mw(H_2O)-F_{989}=0$$

Energy Balance

Overall

$$(F_{986}^{(CO)}/M^{(CO)}H_{986}^{(CO)}+F_{987}^{(DME)}/M^{(DME)}H_{987}^{(DME)}+F_{988}^{(MeOH)}/M^{(MeOH)}H_{988}^{(MeOH)}$$

$$+F_{989}^{(H_2O)}/M^{(H_2O)}H_{989}^{(H_2O)})-(F_{984}^{(CO_2)}/M^{(CO_2)}H_{984}^{(CO_2)}+F_{985}^{(H_2)}/M^{(H_2)}H_{985}^{(H_2)})$$

$$+Q_{out}F_{987}^{(DME)}-Q_{DME}=0$$

Enthalpy Function

$$H_k^i(T)=(a_1^i+\frac{1}{2}a_2^iT+\frac{1}{3}a_3^iT^2+\frac{1}{4}a_4^iT^3+\frac{1}{5}a_5^iT^4+\frac{b_1^i}{T})RT \quad \text{J/mol}$$

i = CO_2, H_2, CO, DME, H_2O

k = 984, 985, 986, 987, 989

$$H_k^{(MeOH)}(T)=(-238.54)(1000)+(79.225)(T-298.15)\ \text{J/mol k=988}$$

Source: Felder and Roussleu (1986)

4-69), the first equation is for the CO_2 balance; the second one is for the H_2 balance; the third one is for the CO balance; the fourth one is for the DME balance; the fifth one is for the methanol balance; the last one is for the H_2O balance.

In the overall energy balance, Q_{DME} is heat input of the new DME process in the form of steam in heat exchanger and distillation column reboilers for heating reactants and product separation, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in heat exchanger and distillation column condensers for cooling reactants and product separation in the new DME process based on the unit of DME product, 5.9 MJ per lb of DME (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 6 variables and 7 equations including two dependent equations (overall material balance and CO_2 balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 19 variables and 14 equations including the dependent overall material balance and CO_2 balance, so the number of degrees of freedom is 7.

C-11. Graphite and Hydrogen (New process) (Speight, 2002; Arakawa, 1998; Motiei, et al., 2001; Nishiguchi, et al., 1998; Indala, 2004)

Graphite is a soft crystalline form of carbon different from amorphous carbon and diamond. Currently, graphite is produced from retort or petroleum coke at about 2,700ºC where the amorphous carbon is processed into graphite (Speight, 2002). Meanwhile, there are some new experimental methods consuming CO_2 for the production of graphite.

Arakawa (1998) described an experimental process for graphite production from carbon dioxide CO by direct hydrogenation over a WO_3 or Y_2O_3 catalyst at 700ºC and 0.1 MPa. The feed gas composition was $H_2/CO_2/N_2 = 2/1/5$. The conversion of carbon dioxide was 60% and the selectivity to graphite was 40%.

Motiei, et al. (2001) reported a laboratory process for synthesizing carbon nanotubes and nested fullerenes, along with graphite, from supercritical CO_2 at 1,000°C and 1,000 MPa with 16% yield of carbonaceous materials. But 59% of the gases leaked out during the reaction because of the high pressure involved.

The above two new methods can not compete with the potentially new process described by Nishiguchi, et al. (1998) based on process ecomomic evaluation, which is discussed in detail in the following section (Indala, 2004).

Since there was no available production capacity for graphite in Louisiana Chemical & Petroleum Products List (1998), a typical production capacity of 100 million pounds per year was taken as a basis. Hence, the capacity of the new process for graphite was set to be 46,000 metric tons per year (Indala, 2004).

C-11-1. Process Description

Nishiguchi, et al. (1998) described an experimental process for the production of graphite by catalytic reduction of carbon dioxide with methane as an intermediate over Ni supported on SiO_2 catalyst. Two-stage reaction mechanism was provided: recycled methane decomposed into graphite carbon and hydrogen, and hydrogen treated with CO_2 to produce methane and water (Equation 4-81, 4-25 and 4-82). The operating condition was 500ºC, atmospheric pressure, and the feed gas composition $H_2/CO_2/N_2 = 4/1/3$. The conversion of CO_2 to graphite carbon was 70%.

$$2CH_4 \rightarrow 2C + 4H_2 \qquad \Delta H^o = 150 \text{ KJ/mol}, \Delta G^o = 101 \text{ KJ/mol} \qquad (4\text{-}81)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \Delta H^o = -165 \text{ KJ/mol}, \Delta G^o = -113 \text{ KJ/mol} \qquad (4\text{-}25)$$

$$CH_4\,(g) + CO_2\,(g) \rightarrow 2C\,(s) + 2H_2O\,(l) \qquad \text{overall reaction} \qquad (4\text{-}82)$$

Compared with the convention process, the new process (500ºC) has much lower temperature than the conventional process (2,700ºC). High CO_2 conversion (70%) and the stable catalyst activity makes the new process competitive with the conventional process and included in the chemical complex.

The block flow diagram is given in Figure 4.30 with stream definitions from Table 4-90.

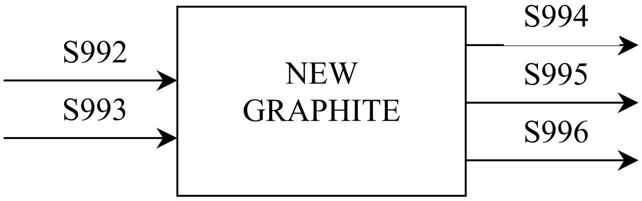


Figure 4.30 Block Diagram of New Graphite Process

Table 4-90 Description of Process Streams in New Graphite Process

Name of Streams	Description
Input Steams	
S992	CH_4 to new graphite process
S993	CO_2 to new graphite process
Output Streams	
S994	H_2 produced from new graphite process
S995	Graphite produced from new graphite process
S996	Water produced from new graphite process

C-11-2. Material Balance and Energy Balance

Using the parameters in Table 4-91, the material balance and energy balance of new graphite process are given in Table 4-92.

Table 4-91 Parameters in New Graphite Production, from Nishiguchi, et al. (1998) and Indala (2004)

Name	Meaning	Value
MCR	Weight ratio of CH_4 to CO_2 in the feedstock in the new graphite process	0.54
	Overall CH_4 conversion rate in new graphite process	1
	Overall CO_2 conversion rate in new graphite process	1

Table 4-92 Constraint Equations for New Graphite Production

Material Balance	
Overall	$(F_{992} + F_{993}) - (F_{994} + F_{995} + F_{996}) = 0$
Species	C: $(\frac{F_{992}}{mw(CH_4)} + \frac{F_{993}}{mw(CO_2)})mw(C) - F_{995} = 0$
	H_2: $F_{994} - (\frac{2F_{995}}{mw(C)} - \frac{4F_{993}}{mw(CO_2)})mw(H_2) = 0$
	H_2O: $\frac{2F_{993}}{mw(CO_2)} mw(H_2O) - F_{996} = 0$
	CO_2: $F_{992} - F_{993}(MCR) = 0$
Energy Balance	
Overall	$(F_{994}^{(H_2)} / M^{(H_2)} H_{994}^{(H_2)} + F_{995}^{(C)} / M^{(C)} H_{995}^{(C)} + F_{996}^{(H_2O)} / M^{(H_2O)} H_{996}^{(H_2O)})$ $- (F_{992}^{(CH_4)} / M^{(CH_4)} H_{992}^{(CH_4)} + F_{993}^{(CO_2)} / M^{(CO_2)} H_{993}^{(CO_2)}) + Q_{out} F_{995}^{(C)} - Q_{GH} = 0$
Enthalpy Function	$H_k^i(T) = (a_1^i + \frac{1}{2}a_2^i T + \frac{1}{3}a_3^i T^2 + \frac{1}{4}a_4^i T^3 + \frac{1}{5}a_5^i T^4 + \frac{b_1^i}{T})RT$ J/mol i = CH_4, CO_2, H_2, C, H_2O k = 992, 993, 994, 995, 996

In Table 4-92, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equations (4-81, 4-25 and 4-82), the first equation is for the graphite balance; the second one is for the H_2 balance; the third one is for the H_2O balance; the last one is for the CO_2 balance.

In the overall energy balance, Q_{GH} is heat input of the new graphite process in the form of steam in heat exchanger and distillation column reboilers for heating reactants and product separation, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in heat exchanger and distillation column condensers for cooling reactants and product separation in the new graphite process based on the unit of graphite product, 11.4 MJ per lb of graphite (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 5 variables and 5 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 16 variables and 11 equations including the dependent overall material balance, so the number of degrees of freedom is 6.

C-12. Hydrogen (New Process) (Speight, 2002; Song, et al., 2002; Inui, 2002; Wei, et al., 2002; Nakagawa, et al., 2002; Effendi, et al., 2002; Tomishige, et al., 1998; Shamsi, 2002; Indala, 2004; Louisiana Chemical & Petroleum Products List, 1998)

To provide H_2 needed in the potentially new processes consuming CO_2 in the previous sections, the H_2 sources will be discussed here. The commercial process for hydrogen production is steam reforming of natural gas involving reforming and shift conversion (Equation 4-21 and 4-22). Desulfurized natural gas is mixed with steam over a nickel catalyst in a reforming furnace at 760-980ºC and 4.1 MPa (Speight, 2002). Formed gas mixture of CO and H_2 enters a shift converter where carbon monoxide reacts with more steam to produce hydrogen and CO_2 over iron or chromic oxide catalysts at 425ºC. The product mixture gas of CO_2 and H_2 are separated using monoethanolamine absorbing and desorbing CO_2 (Speight, 2002).

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H^o = 206 \text{ KJ/mol}, \Delta G^o = 142 \text{ KJ/mol} \quad (4\text{-}21)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H^o = -41 \text{ KJ/mol}, \Delta G^o = -29 \text{ KJ/mol} \quad (4\text{-}22)$$

There are many experimental processes consuming CO_2 to produce either pure H_2 or synthesis gas through reforming of methane, which is a good source of H_2 for the chemical complex. Some of these potentially new processes are reviewed here.

Song, et al. (2002) gave the new process to produce CO rich synthesis gas from CO_2 reforming of methane over Ni/Al_2O_3 catalyst at 750ºC and 1 atm with equimolar methane and CO_2 input (Equation 4-83). The results were 91.8% CO_2 conversions, 95.3% CH_4 conversion, 82% CO yield, 66% H_2 yield, and product composition of $H_2/CO = 0.81$.

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \quad \Delta H^o = 247 \text{ KJ/mol}, \Delta G^o = 171 \text{ KJ/mol} \quad (4\text{-}83)$$

Inui (2002) discussed the catalyst role in the production of synthesis gas through CO_2 reforming of methane. The highest CH_4 conversion rate was 82.2% over a Rh-modified four-component catalyst at 700ºC and 1 atm. The observed conversion of methane was 80.8%.

Wei, et al. (2002) described an experimental process of reforming methane to synthesis gas through over Ni supported ultra fine ZrO_2 catalyst at 757°C and 1atm with equimolar CH_4 and CO_2 input (Equation 4-83). There was no deactivation of the catalyst for over 600 hours. The results were 88.3% CO_2 conversions, 86.2% CH_4

conversion, 95.4% CO selectivity, 66% H_2 selectivity, and product composition of $H_2/CO = 0.83$.

Nakagawa, et al. (2002) reported a new process for synthesis gas production by reforming methane over a Ru loaded Y_2O_3 catalyst at 600°C and 1 atm with equimolar CH_4 and CO_2 input (Equation 4-83). The results were 35.5% CO_2 conversions, 30% CH_4 conversion, 32.7% CO yield, 27% H_2 yield, and product composition of $H_2/CO = 0.83$.

Effendi, et al. (2002) described an experimental process for reforming methane to synthesis gas over Ni/SiO_2-MgO catalyst at 700°C and 1 atm with the feed gas composition $CO_2/CH_4 = 0.84$ (Equation 4-83). The conversions of CH_4 and CO_2 were 37.7% and 52.7%, respectively, and synthesis gas composition was $H_2/CO = 0.69$.

Tomishige, et al. (1998) described a laboratory process by reforming methane for the production of synthesis gas over a nickel-magnesia solid solution catalyst at 850°C and 0.1 MPa with equimolar of CH_4 and CO_2 input (Equation 4-83). The conversion of methane was 80%. Meanwhile, the catalyst was inexpensive compared to the other commercial catalysts, and was effective in preventing the coke deposition inside the reactor (Tomishige, et al., 1998).

According process evaluation by Indala (2004), the above new processes for the production of synthesis gas could not compete with the potentially new process described by Shamsi (2002) which is discussed in the following section and included in the chemical complex as a H_2 source.

The process production capacity was set to be 13,400 metric tons of H_2 per year. This was based on a hydrogen plant of Air Products and Chemicals Inc., located in Geismar, LA, with the capacity of 15 million cubic feet per day (Louisiana Chemical & Petroleum Products List, 1998).

C-12-1. Process Description

Shamsi (2002) reported three laboratory processes of CO_2 reforming methane to produce synthesis gas over three different catalysts. The best reaction condition was at 850ºC and 1 atm over a noble metal catalyst of 1% rhodium supported on alumina in a fixed bed reactor (Equation 4-83). The conversions of methane and CO_2 were both 97%. The reported yield of CO was 96% with equimolar products of CO and H_2.

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \qquad \Delta H^o = 247 \text{ KJ/mol}, \Delta G^o = 171 \text{ KJ/mol} \quad (4\text{-}83)$$

Compared with the conventional process, the new process (850ºC) operates in the same temperature range as the conventional process (760-980ºC). But, the new one (0.1 MPa) operates very lower pressure than the conventional process (4.1 MPa). On the other hand, the new process had the competitive high yields of the products with better performance catalysts. Hence, the potentially new process was selected for the HYSYS simulation and included in the chemical complex.

The block flow diagram is given in Figure 4.31 with stream definitions from Table 4-93.

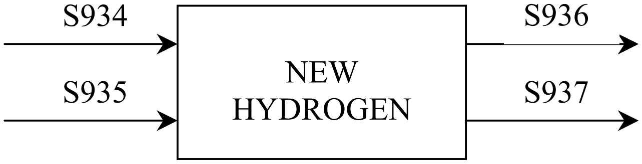


Figure 4.31 Block Diagram of New Hydrogen Process

Table 4-93 Description of Process Streams in New Hydrogen Process

Name of Streams	Description
Input Steams	
S934	CH_4 to new hydrogen process
S935	CO_2 to new hydrogen process
Output Streams	
S936	H_2 produced from new hydrogen process
S937	CO produced from new hydrogen process

C-12-2. Material Balance and Energy Balance

Using the parameters in Table 4-94, the material balance and energy balance of new hydrogen process are given in Table 4-95.

In Table 4-95, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equations (4-83), the first equation is for the CH_4 balance; the second one is for the CO_2 balance; the last one is for the CO balance.

In the overall energy balance, Q_{SYNGC} is heat input of the new hydrogen process in the form of steam in heat exchanger and distillation column reboilers for heat supply of the endothermic reaction and product separation, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in distillation column condensers for product separation in the new hydrogen process based on the unit of hydrogen product, 1.4 MJ per lb of hydrogen (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 4 variables and 4 equations including one dependent equation (overall material balance), so the number of degrees of freedom is

1. For the material and energy balance, there are 13 variables and 9 equations including the dependent overall material balance, so the number of degrees of freedom is 5.

Table 4-94 Parameters in New Hydrogen Production, from Shamsi (2002) and Indala (2004)

Name	Meaning	Value
	Overall CH_4 conversion rate in new graphite process	1
	Overall CO_2 conversion rate in new graphite process	1
	H_2 selectivity in new hydrogen process	1

Table 4-95 Constraint Equations for New Hydrogen Production

Material Balance	
Overall	$(F_{934} + F_{935}) - (F_{936} + F_{937}) = 0$
Species	CH_4: $F_{934} - \frac{F_{936}}{2mw(H_2)} mw(CH_4) = 0$
	CO_2: $F_{935} - \frac{F_{936}}{2mw(H_2)} mw(CO_2) = 0$
	CO: $\frac{F_{936}}{mw(H_2)} mw(CO) - F_{937} = 0$
Energy Balance	
Overall	$(F_{936}^{(H_2)} / M^{(H_2)} H_{936}^{(H_2)} + F_{937}^{(CO)} / M^{(CO)} H_{937}^{(CO)}) - (F_{934}^{(CH_4)} / M^{(CH_4)} H_{934}^{(CH_4)}$
	$+ F_{935}^{(CO_2)} / M^{(CO_2)} H_{935}^{(CO_2)}) + Q_{out} F_{936}^{(H_2)} - Q_{SYNGC} = 0$
Enthalpy Function	$H_k^i(T) = (a_1^i + \frac{1}{2} a_2^i T + \frac{1}{3} a_3^i T^2 + \frac{1}{4} a_4^i T^3 + \frac{1}{5} a_5^i T^4 + \frac{b_1^i}{T}) RT$ J/mol
	i = CH_4, CO_2, H_2, CO
	k = 934, 935, 936, 937

C-13. Propylene (New Processes) (Pellegrino, 2000; Speight, 2002; Wells, 1999; Takahara, et al., 1998; Indala, 2004; C & EN, 2003; Louisiana Chemical & Petroleum Products List, 1998)

Propylene has a potential energy savings of 98 trillion BTUs per year though improved catalysts (Pellegrino, 2000). The conventional production of propylene is the steam cracking of hydrocarbons. Propane, naphtha, or gas oil is used as a feedstock and propylene and ethylene are co-products (Speight, 2002). 70% of world propylene production is obtained as co-product from naphtha cracking, with 2% from propane and the remainder from refinery operations and dehydrogenation (Wells, 1999). The overall chemical reaction using propane as feedstock (Equation 4-84) takes place at a temperature of 750-870°C and 31-37 atm, with the propylene yield 14-18% and the ethylene yield 42-45% (Wells, 1999).

$$2C_3H_8 \rightarrow C_3H_6 + C_2H_4 + CH_4 + H_2 \quad \Delta H^o = 205.5 \text{ KJ/mol}, \Delta G^o = 127.5 \text{ KJ/mol} \quad (4\text{-}84)$$

Two new processes for propylene production are discussed and included in the chemical complex after HYSYS simulation, one from dehydrogenation of propane using CO_2, and the other from dehydrogenation of propane. The first one consumes carbon dioxide and the other is a source of hydrogen for hydrogenation of carbon dioxide.

C-13-1. Propane Dehydrogenation by CO_2 (New Propylene by CO_2) (Takahara, et al., 1998; Indala, 2004; Louisiana Chemical & Petroleum Products List, 1998)

The process production capacity was set to be 41,900 metric tons of propylene per year. This was based on a plant of Union Texas Ethylene Corporation, located in Geismar, LA, with the capacity of 92 million pounds propylene per year (Louisiana Chemical & Petroleum Products List, 1998).

C-13-1-1. Process Description

Takahara, et al. (1998) described a new laboratory process by dehydrogenation of propane using carbon dioxide for the synthesis of propylene over Cr_2O_3/SiO_2

catalyst at 550°C and 1 atm (Equation 4-85). The major by-products were CO and H_2. The conversion of propane was 45% and the yield to propylene was 10 %.

$$2C_3H_8 + CO_2 \rightarrow 2C_3H_6 + CO + H_2O + H_2 \quad \Delta H^o = 289 \text{ kJ/mol}, \Delta G^o = 201 \text{ kJ/mol} \quad (4\text{-}85)$$

Compared with the conventional process, the reaction condition of the new process (550°C and 1 atm) is much milder than that of the conventional process (750-870°C and 31-37 atm). The yield of propylene in the new process (10%) is comparable with that of the conventional process (14-18%). On the other hand, CO_2 feedstock from other process emissions can suppresses catalyst deactivation in the new process. Hence, this new process was simulated with HYSYS and included in the chemical complex. The block flow diagram is given in Figure 4.32 with stream definitions from Table 4-96.

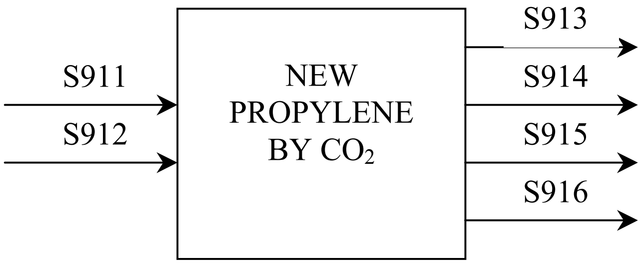


Figure 4.32 Block Diagram of New Propylene by CO_2 Process

Table 4-96 Description of Process Streams in New Propylene by CO_2 Process

Name of Streams	Description
Input Steams	
S911	Propane to new propylene by CO_2 process
S912	CO_2 to new propylene by CO_2 process
Output Streams	
S913	CO produced new propylene by CO_2 process
S914	Propylene produced from new propylene by CO_2 process
S915	Water produced from new propylene by CO_2 process
S916	H_2 produced from new propylene by CO_2 process

C-13-1-2. Material Balance and Energy Balance

Using the parameters in Table 4-97, the material balance and energy balance of new propylene by CO_2 process are given in Table 4-98.

Table 4-97 Parameters in New Propylene Production by CO_2, from Takahara, et al. (1998) and Indala (2004)

Name	Meaning	Value
	Overall propane conversion rate in new propylene by CO_2 process	1
	Propylene selectivity in new propylene by CO_2 process	1

Table 4-98 Constraint Equations for New Propylene Production by CO_2

Material Balance	
Overall	$(F_{911}+F_{912})-(F_{913}+F_{914}+F_{915}+F_{916})=0$
Species	C_3H_8: $F_{911}-\frac{F_{914}}{mw(C_3H_6)}mw(C_3H_8)=0$
	CO_2: $\frac{F_{914}}{2mw(C_3H_6)}mw(CO_2)-F_{912}=0$
	H_2: $\frac{F_{914}}{2mw(C_3H_6)}mw(H_2)-F_{916}=0$
	CO: $\frac{F_{914}}{2mw(C_3H_6)}mw(CO)-F_{913}=0$
	H_2O: $\frac{F_{914}}{2mw(C_3H_6)}mw(H_2O)-F_{915}=0$
Energy Balance	
Overall	$(F_{913}^{(CO)}/M^{(CO)}H_{913}^{(CO)}+F_{914}^{(C_3H_6)}/M^{(C_3H_6)}H_{914}^{(C_3H_6)}+F_{915}^{(H_2O)}/M^{(H_2O)}H_{915}^{(H_2O)}$ $+F_{916}^{(H_2)}/M^{(H_2)}H_{916}^{(H_2)})-(F_{911}^{(C_3H_8)}/M^{(C_3H_8)}H_{911}^{(C_3H_8)}+F_{912}^{(CO_2)}/M^{(CO_2)}H_{912}^{(CO_2)})$ $+Q_{out}F_{914}^{(C_3H_6)}-Q_{PPEN}=0$
Enthalpy Function	$H_k^i(T)=(a_1^i+\frac{1}{2}a_2^iT+\frac{1}{3}a_3^iT^2+\frac{1}{4}a_4^iT^3+\frac{1}{5}a_5^iT^4+\frac{b_1^i}{T})RT$ J/mol i = C_3H_8, CO_2, CO, C_3H_6, H_2O, H_2 k = 911, 912, 913, 914, 915, 916

In Table 4-98, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equations (4-85), the first equation is for the C_3H_8 balance; the second one is for the CO_2 balance; the third one is for the H_2 balance; the fourth one is for the CO balance; the last one is for the H_2O balance.

In the overall energy balance, Q_{PPEN} is heat input of the new propylene by CO_2 process in the form of steam in heat exchanger and distillation column reboilers for heat supply of the endothermic reaction and product separation, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in heat exchanger and distillation column condensers for product separation in the new propylene by CO_2 process based on the unit of propylene product, 3.2 MJ per lb of propylene (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 6 variables and 6 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 19 variables and 13 equations including the dependent overall material balance, so the number of degrees of freedom is 7.

C-13-2. Propane Dehydrogenation (C & EN, 2003; Indala, 2004; Louisiana Chemical & Petroleum Products List, 1998)

The process production capacity was set to be 41,800 metric tons of propylene per year. This was based on a plant of Union Texas Ethylene Corporation, located in

Geismar, LA, with the capacity of 92 million pounds propylene per year (Louisiana Chemical & Petroleum Products List, 1998).

C-13-2-1. Process Description

The world largest propane dehydrogenation plant for propylene production, which was built and operated by BASF Sonatrac PropanChem S.A., has started its trial operations at Tarragona, Spain (Equation 4-86) (C & EN, 2003). It is the first plant in Europe to use UOP LLC's C_3 Oleflex technology to only produce propylene from propane with the capacity of 350,000 metric tons per year of propylene. The reaction condition is 600°C and 1 atm over a proprietary platinum catalyst from UOP (called DeH-14) with 85% selectivity to propylene and 40% propane conversion per pass (C & EN, 2003).

$$C_3H_8 \rightarrow C_3H_6 + H_2 \qquad \Delta H^o = 124 \text{ kJ/mol}, \Delta G^o = 86 \text{ kJ/mol} \quad (4\text{-}86)$$

Compared with the conventional process (steam cracking), the new process has much milder reaction condition (600°C and 1 atm) than the conventional process (750-870°C and 31-37 atm). No by-product ethylene is produced in the new process with the by-product H_2 that can be used as a feedstock in other CO_2 hydrogenation processes. It is more economical to use the propane dehydrogenation process than the conventional process because only propylene is needed at the Tarragona site and the production cost is at most one fourth of the conventional process (C & EN, 2003). On the other hand, since this new process has already started trial operation with industrial production scale at Tarragona, Spain, this process is more realistic than laboratory scale processes. Meanwhile, there are no such plants in the lower Mississippi River corridor that uses this new process, so this process is simulated with HYSYS and incorporated into the chemical complex.

The block flow diagram is given in Figure 4.33 with stream definitions from Table 4-99.

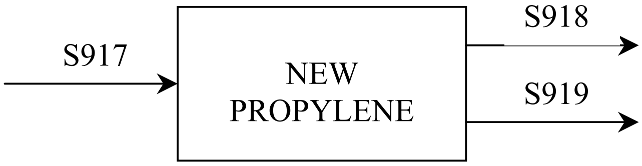


Figure 4.33 Block Diagram of New Propylene Process

Table 4-99 Description of Process Streams in New Propylene Process

Name of Streams	Description
Input Steams	
S917	Propane to new propylene process
Output Streams	
S918	H_2 produced from new propylene process
S919	Propylene produced from new propylene process

C-13-2-2. Material Balance and Energy Balance

Using the parameters in Table 4-100, the material balance and energy balance of new propylene process are given in Table 4-101.

In Table 4-101, the overall material balance for the whole process is given first. For the species material balance obtained using the reaction equations (4-86), the first equation is for the C_3H_8 balance; the second one is for the H_2 balance.

In the overall energy balance, Q_{PPEND} is heat input of the new propylene process in the form of steam in heat exchanger and distillation column reboilers for the heat supply for the endothermic reaction and product separation, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in heat exchanger and distillation column condensers for product separation in the new propylene process based on the unit of propylene product, 5.8 MJ per lb of propylene (Indala, 2004). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 3 variables and 3 equations including one dependent equation (overall material balance), so the number of degrees of freedom is 1. For the material and energy balance, there are 10 variables and 7 equations including the dependent overall material balance, so the number of degrees of freedom is 4.

Table 4-100 Parameters in New Propylene Production, from C & EN (2003) and Indala (2004)

Name	Meaning	Value
	Overall propane conversion rate in new propylene process	1
	Propylene selectivity in new propylene process	1

Table 4-101 Constraint Equations for New Propylene Production

Material Balance	
Overall	$F_{917} - (F_{918} + F_{919}) = 0$
Species	C_3H_8: $F_{917} - \frac{F_{919}}{mw(C_3H_6)} mw(C_3H_8) = 0$
	H_2: $\frac{F_{919}}{mw(C_3H_6)} mw(H_2) - F_{918} = 0$
Energy Balance	
Overall	$(F_{918}^{(H_2)} / M^{(H_2)} H_{918}^{(H_2)} + F_{919}^{(C_3H_6)} / M^{(C_3H_6)} H_{919}^{(C_3H_6)}) - F_{917}^{(C_3H_8)} / M^{(C_3H_8)} H_{917}^{(C_3H_8)}$ $+ Q_{out} F_{919}^{(C_3H_6)} - Q_{PPEND} = 0$
Enthalpy Function	$H_k^i(T) = (a_1^i + \frac{1}{2}a_2^i T + \frac{1}{3}a_3^i T^2 + \frac{1}{4}a_4^i T^3 + \frac{1}{5}a_5^i T^4 + \frac{b_1^i}{T})RT$ J/mol i = C_3H_8, H_2, C_3H_6 k = 917, 918, 919

C-14. Sulfuric Acid (Superstructure) (Hertwig, 2004)

Because there were S and SO_2 from two gypsum reuse processes (Process C-3-1 and C-3-2) as feedstocks to sulfuric acid plant in the superstructure, these streams were added as input streams compared to the process in the base case with the corresponding mass and energy balance changes given in this section.

C-14-1. Process Description of Contact Process for Sulfuric Acid

The block diagram is shown in Figure 4.34 with the stream definitions in Table 4-102.

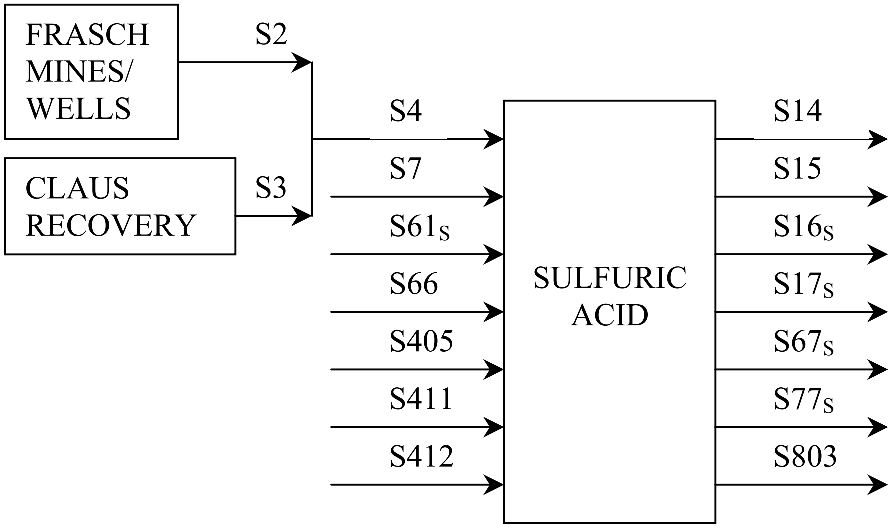


Figure 4.34 Block Diagram of Contact Process to Produce Sulfuric Acid (Superstructure)

C-14-2. Material Balance and Energy Balance

The material balance and energy balance equations for this process are given in Table 4-103. The only changes compared with the one in base case are the input of S and SO_2 from two gypsum reuse process.

In the material balance part, there are 26 variables and 23 equations including one dependent one (overall material balance). So the number of degrees of freedom is 4 for the material balance part. For the material and energy balance, there are 38 variables and 29 equations including the dependent overall material balance. The number of degrees of freedom is 10.

Table 4-102 Description of Process Streams in Contact Sulfuric Acid Production (Superstructure)

Name of Streams	Description
Input Streams	
S2	S from Frasch mines/wells to sulfuric acid process (SAP)
S3	S from Claus recovery to SAP
S4	Total S to SAP
S7	Dry air to SAP
$S61_S$	boiler feed water (BFW) to SAP
S66	Process water to SAP
S405	SO_2 from sulfuric dioxide recovery process
S411	SO_2 from sulfur and sulfur dioxide recovery process
S412	S from sulfur and sulfur dioxide recovery process
Output Streams	
S14	H_2SO_4 solution produced from SAP
S15	Vent gases exiting from SAP
$S16_S$	Low pressure steam (LP) (40 psig) exiting from SAP
$S17_S$	High pressure steam (HP) (600 psig) exiting from SAP
$S67_S$	Boiler blowdown H_2O from SAP
$S77_S$	Intermediate pressure steam (IP) (150 psig) exiting from SAP
S803	Impurity of sulfur from SAP

Table 4-103 Constraint Equations for Contact Sulfuric Acid Production (Superstructure)

Material Balances	
Overall	$(F_4 + F_7 + F_{S61} + F_{66} + F_{405} + F_{411} + F_{412})$ $-(F_{14} + F_{15} + F_{S16} + F_{S17} + F_{S67} + F_{S77} + F_{803}) = 0$ where $F_7 = F_7^{(O_2)} + F_7^{(N_2)} + F_7^{(CO_2)} + F_7^{(Ar)}$ $F_{14} = F_{14}^{(H_2SO_4)} + F_{14}^{(H_2O)}$ $F_{15} = F_{15}^{(N_2)} + F_{15}^{(Ar)} + F_{15}^{(CO_2)} + F_{15}^{(SO_2)}$

Table 4-103 Continued

Material Balance (Continued)

Heat Exchange (boiler feed water and steam balance)

$$(F_{S16} + F_{S17} + F_{S67} + F_{S77}) - F_{S61} = 0$$

$$F_{S61} = F_{S61}^{(a)} + F_{S61}^{(b)}$$

Species

$$S: \begin{aligned}&(F_4(1 - SIPSA) + F_{412} + \frac{32.06}{64.06}(F_{405} + F_{411})) - \frac{32.06}{98.08}F_{14}^{(H_2SO_4)}\\ &- \frac{32.06}{64.06}F_{15}^{(SO_2)} = 0\end{aligned}$$

$$H_2O(\text{process water}): F_{66} - \frac{18.02}{98.08}F_{14}^{(H_2SO_4)} - F_{14}^{(H_2O)} = 0$$

$$O_2: F_7^{(O_2)} + \frac{32}{64.06}(F_{405} + F_{411}) - (1.5)\frac{32}{98.08}F_{14}^{(H_2SO_4)} - \frac{32}{64.06}F_{15}^{(SO_2)} = 0$$

$$N_2: F_{15}^{(N_2)} - F_7^{(N_2)} = 0$$

$$Ar: F_{15}^{(Ar)} - F_7^{(Ar)} = 0$$

$$CO_2: F_{15}^{(CO_2)} - F_7^{(CO_2)} = 0$$

$$SO_2: \frac{SO2EMSA}{2000}F_{14}^{(H_2SO_4)} - F_{15}^{(SO_2)} = 0$$

$$\text{Impurity: } F_{803} = F_4 \times SIPSA$$

Heat Exchange

$$\text{BFW: } F_{S61}^{(a)} - \frac{(F_{S16} + F_{S17})}{(1 - BBLSA)} = 0$$

$$\text{HP: } F_{S17} - \frac{(12)(1 - HPBTSA)}{SHPSA}F_{14}^{(H_2SO_4)} = 0$$

$$\text{IP: } F_{S77} - \frac{IPCAPSA \times IPHRSSA(12)}{(3400)}F_{14}^{(H_2SO_4)} = 0$$

$$\text{LP: } F_{S16} - \frac{(12)HPBTSA}{SHPSA}F_{14}^{(H_2SO_4)} = 0$$

$$\text{Blowdown } H_2O\text{: } F_{S67} = BBLSA \times F_{S61}^{(a)}$$

Energy Balance

Overall

$$\begin{aligned}&(\frac{1}{M^{(H_2O)}}F_{S61}^{(H_2O)}H_{S61}^{(H_2O)} - (F_{S16}H^{(LP)} + F_{S17}H^{(HP)} + F_{S77}H^{(IP)}\\ &+ \frac{1}{M^{(H_2O)}}F_{S67}^{(H_2O)}H_{S67}^{(H_2O)})) - Q_{SACID} = 0\end{aligned}$$

where M^i is molecule weight, $i = H_2O$

Table 4-103 Continued

Energy Balance (Continued)	
Enthalpy Function	$H_k^i(T)=(a_1^i+\frac{1}{2}a_2^iT+\frac{1}{3}a_3^iT^2+\frac{1}{4}a_4^iT^3+\frac{1}{5}a_5^iT^4+\frac{b_1^i}{T})RT$ J/mol where R is gas constant T is temperature $i = H_2O$ $k = 61, 67$ $H^{(LP)}(T)=((72.558+(0.5)(-0.66244)T+(\frac{1}{3})(0.002562)T^2+(0.25)(-4.3659E-06)T^3+(0.2)(2.7818E-09)T^4+\frac{(-41886)}{T})(8.3145)T-1893)\frac{1}{18.02}+((-0.007)T^2+(2.7838)T+2292.0563)$ J/g $H^{(IP)}(T)=((72.558+(0.5)(-0.66244)T+(\frac{1}{3})(0.002562)T^2+(0.25)(-4.3659E-06)T^3+(0.2)(2.7818E-09)T^4+\frac{(-41886)}{T})(8.3145)T-1893)\frac{1}{18.02}+((-0.007)T^2+(2.7838)T+2292.0563)$ J/g $H^{(HP)}(P,T)=2.326((5.32661)((T-273.15)(1.8)+32)-0.2839015P-(7.352389E-03)((T-273.15)(1.8)+32)^2+(3.581547E-06)((T-273.15)(1.8)+32)^3-(7.289244E-05)P^2+(4.595405E-04)((T-273.15)(1.8)+32)P)-15861.82$ J/g, P:psia Note: LP and IP have no super heat, from Meyer, et al. (1977) and McBride, et al. (1993); HP has super heat, from Chen (1998).

C-15. Granular Triple Super Phosphate (GTSP) (Superstructure) (Hertwig, 2004; Brown, et al., 1985)

C-15-1. Process Description

Because there were phosphoric acid from electric furnace (Process C-1) and Haifa (Process C-2) processes as feedstock to the GTSP process in the superstructure, these streams were added as input streams compared to the process in the base case with the corresponding mass and energy balance changes given in this section. The block diagram is given in Figure 4.35 with the stream descriptions from Table 4-104.

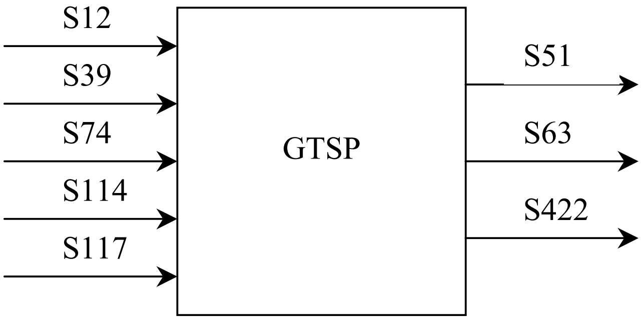


Figure 4.35 Block Diagram of GTSP Plant (Superstructure)

Table 4-104 Description of Process Streams in GTSP Plant (Superstructure)

Name of Stream	Description
Input Streams	
S12	Phosphate rock to GTSP
S39	Wet process phosphorous acid to GTSP
S74	Inert impurity to GTSP
S114	Electric furnace H_3PO_4 to GTSP
S117	Haifa H_3PO_4 to GTSP
Output Streams	
S51	GTSP produced from GTSP
S63	HF produced from GTSP
S422	Water evaporated from GTSP

C-15-2. Material Balance and Energy Balance

The material balance and energy balance equations for this process are given in Table 4-105. The only changes compared with the one in base case are the input of phosphoric acid from electric furnace and Haifa processes.

Table 4-105 Constraint Equations for GTSP Production (Superstructure)

Material Balance	
Overall	$(F_{12}+F_{39}+F_{74}+F_{114}+F_{117})-(F_{51}+F_{63}+F_{422})=0$
	where
	$F_{12}=F_{12}^{(ROCK)}$
	$F_{39}=F_{39}^{(P_2O_5)}+F_{39}^{(H_2O)}$
	$F_{114}=F_{114}^{(P_2O_5)}+F_{114}^{(H_2O)}$
	$F_{117}=F_{117}^{(P_2O_5)}+F_{117}^{(H_2O)}$
Species	P_2O_5: $\frac{UPAGTSP}{\frac{141.94}{(2)(98)}}(F_{39}^{(P_2O_5)}+F_{114}^{(P_2O_5)}+F_{117}^{(P_2O_5)})-\frac{(PGTSP)(14)(98)}{\frac{141.94}{234.06}(10)(234.06)}F_{51}=0$
	ROCK:
	$F_{12}^{(ROCK)}-\frac{(UPAGTSP)(2)(98)(1008.62)(100)(3)(310.18)}{(141.94)(14)(98)(BPLGTSP)(1008.62)(URGTSP)}(F_{39}^{(P_2O_5)}+F_{114}^{(P_2O_5)}$
	$+F_{117}^{(P_2O_5)})=0$
	HF: $\frac{(UPAGTSP)(2)(98)(2)(20.01)}{(141.94)(14)(98)}(F_{39}^{(P_2O_5)}+F_{114}^{(P_2O_5)}+F_{117}^{(P_2O_5)})-F_{63}=0$
	H_2O: $F_{422}-((F_{39}^{(H_2O)}+F_{114}^{(H_2O)}+F_{117}^{(H_2O)})-\frac{(3)(18.02)}{141.94}(F_{39}^{(P_2O_5)}+F_{114}^{(P_2O_5)}+F_{117}^{(P_2O_5)})=0$
Energy Balance	
Overall	$((PGTSP)F_{51}^{(GTSP)}/M^{(P_2O_5)}H^{(GTSP)}+F_{63}^{(HF)}/M^{(HF)}H_{63}^{(HF)}+F_{422}^{(H_2O)}/M^{(H_2O)}H_{422}^{(H_2O)})$
	$-((BPLGTSP)/(100)F_{12}^{(ROCK)}/((3)M^{(Ca_3(PO)_4)})H^{(ROCK)}+$
	$\Sigma(F_{39}^{(i)}+F_{114}^{(i)}+F_{117}^{(i)})/M^{(i)}H^{(i)})+F_{51}Q_{out}-Q_{GTSP}=0$
	$i = P_2O_5, H_2O$
Enthalpy Function	$H_k^i(T)=(a_1^i+\frac{1}{2}a_2^iT+\frac{1}{3}a_3^iT^2+\frac{1}{4}a_4^iT^3+\frac{1}{5}a_5^iT^4+\frac{b_1^i}{T})RT$ J/mol
	$i = H_2O, HF$
	$k = 39, 63, 114, 117, 422$
	$H^{(ROCK)}(T)=(((-291.5)(1000)+(3)(-984.9)(1000))+(16.02+(3)(54.45))$
	$(T-298.15))(4.182)J/mol$
	Source: Lide (1982)
	$H^{(P_2O_5)}=(-1278.437)(1000)+(106.014)(T-298.15)J/mol$
	Source: Lide (1982)
	$H^{(GTSP)}(T)=(-742.04)(1000)(4.182)+(246.4)(T-298.15)J/mol$
	Source: Felder and Roussleu (1986)

In the material balance part, there are 15 variables and 12 equations, so the number of degrees of freedom is 3. For the material and energy balance, there are 27 variables and 19 equations, so the number of degrees of freedom is 8.

C-16. Mono-/Di-Ammonium Phosphates (MAP/DAP) (Superstructure) (Hertwig, 2004; Brown, et al., 1985; Louisiana Chemical & Petroleum Products List, 1998)

C-16-1. Process Description

Because there were phosphoric acid from electric furnace (Process C-1) and Haifa (Process C-2) processes as feedstock to the MAP and DAP process in the superstructure, these streams were added as input streams compared to the process in the base case with the corresponding mass and energy balance changes given in this section. The block diagram is illustrated in Figure 4.36 with the stream definitions in Table 4-106.

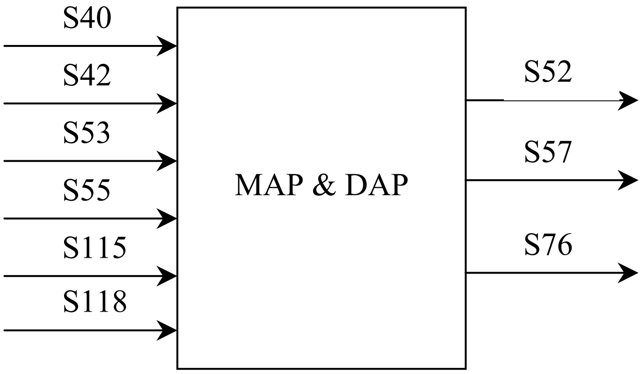


Figure 4.36 Block Diagram of MAP & DAP Plant (Superstructure)

C-16-2. Material Balance and Energy Balance

The material balance and energy balance equations for this process are given in Table 4-107. The only changes compared with the one in base case are the input of phosphoric acid from electric furnace and Haifa processes.

Table 4-106 Description of Process Streams in MAP & DAP Plant (Superstructure)

Name of Streams	Description
Input Streams	
S40	Wet process phosphoric acid to MAP & DAP plant
S42	Ammonia to MAP & DAP plant
S53	Urea produced from urea plant as N-boosters to MAP & DAP plant
S55	Inert impurity to MAP & DAP plant
S115	Electric furnace H_3PO_4 to MAP & DAP plant
S118	H_3PO_4 produced from Haifa process to MAP & DAP plant
Output Streams	
S52	MAP produced from MAP & DAP plant
S57	DAP produced from MAP & DAP plant
S76	Water vapor from MAP & DAP plant

Table 4-107 Constraint Equations for MAP & DAP Production (Superstructure)

Material Balance

Overall

$$(F_{40}+F_{42}+F_{53}+F_{55}+F_{115}+F_{118})-(F_{52}+F_{57}+F_{76})=0$$

where

$$F_{40}=F_{40}^{(P_2O_5)}+F_{40}^{(H_2O)}$$

$$F_{53}=F_{53}^{(UREA)}$$

$$F_{115}=F_{115}^{(P_2O_5)}+F_{115}^{(H_2O)}$$

$$F_{118}=F_{118}^{(P_2O_5)}+F_{118}^{(H_2O)}$$

Species

$$P_2O_5\text{: } (F_{40}^{(P_2O_5)}+F_{115}^{(P_2O_5)}+F_{118}^{(P_2O_5)})-(\frac{P2O5MAP}{100}F_{52}+\frac{P2O5DAP}{100}F_{57})=0$$

NH_3:

$$\begin{aligned}&\frac{1}{17.04}F_{42}-\frac{(RPDAP)(NDAP)}{(RPDAP+RPMAP)(P2O5DAP)(14.01)}(F_{40}^{(P_2O_5)}+F_{115}^{(P_2O_5)}\\&+F_{118}^{(P_2O_5)})-\frac{(RPMAP)(NMAP)}{(RPDAP+RPMAP)(P2O5MAP)(14.01)}(F_{40}^{(P_2O_5)}+F_{115}^{(P_2O_5)}\\&+F_{118}^{(P_2O_5)})=0\end{aligned}$$

$$\text{UREA: } F_{53}^{(UREA)}-(NBRDAP)F_{57}=0$$

H_2O:

$$F_{76}-((F_{40}^{(H_2O)}+F_{115}^{(H_2O)}+F_{118}^{(H_2O)})-\frac{(3)(18.02)}{141.94}(F_{40}^{(P_2O_5)}+F_{115}^{(P_2O_5)}+F_{118}^{(P_2O_5)}))=0$$

Table 4-107 Continued

Material Balance (Continued)	
Species	MAP: $F_{52} - \frac{(\mathrm{RPMAP})(100)}{(\mathrm{RPDAP}+\mathrm{RPMAP})(\mathrm{P2O5MAP})}(F_{40}^{(P_2O_5)} + F_{115}^{(P_2O_5)} + F_{118}^{(P_2O_5)}) = 0$
Energy Balance	
Overall	$((\mathrm{PURMAP})F_{52}^{(MAP)}/M^{(MAP)}H_{52}^{(MAP)} + (\mathrm{PURDAP})F_{57}^{(DAP)}/M^{(DAP)}H_{57}^{(DAP)} +$ $F_{76}^{(H_2O)}/M^{(H_2O)}H_{76}^{(H_2O)}) - (\Sigma F_{40}^{(i)}/M^{(i)}H_{40}^{(i)} + \Sigma F_{115}^{(i)}/M^{(i)}H_{115}^{(i)}$ $+ \Sigma F_{118}^{(i)}/M^{(i)}H_{118}^{(i)} + F_{42}^{(NH_3)}/M^{(NH_3)}H_{42}^{(NH_3)}) + Q_{out}(F_{52} + F_{57}) - Q_{APG} = 0$ i = P_2O_5, H_2O
Enthalpy Function	$H_k^i(T) = (a_1^i + \frac{1}{2}a_2^iT + \frac{1}{3}a_3^iT^2 + \frac{1}{4}a_4^iT^3 + \frac{1}{5}a_5^iT^4 + \frac{b_1^i}{T})RT$ J/mol i = H_2O, NH_3 k = 40, 42, 76, 115, 118 $H^{(P_2O_5)} = (-1278.437)(1000) + 106.014(T - 298.15)\mathrm{J/mol}$ Source: Lide (1982) $H_k^{(MAP)} = ((-345.38)(1000) + 34.00(T - 298.15))4.182$ J/mol k=52 Source: Lide (1982) $H_k^{(DAP)} = ((-374.50)(1000) + 45.00(T - 298.15))4.182$ J/mol k=57 Source: Lide (1982)

In the material balance part, there are 15 variables and 12 equations, so the number of degrees of freedom is 3. For the material and energy balance, there are 27 variables and 19 equations, so the number of degrees of freedom is 8.

C-17. Relations of Chemical Production Complex in the Superstructure

The streams not defined in the above plant models are described in Table 4-108. The stream relationship for mass balance in the superstructure of chemical production complex is given in Table 4-109, and for energy balance is given in Table 4-110.

Table 4-108 Description of Process Streams in the Superstructure

Name of Streams	Description
S5	Total air input to the superstructure
S6	Total natural gas input to the superstructure
Sapply	Steam available for the superstructure
S30	NH_3 from NH_3 plant to ammonium nitrate plant and for sale
S43	NH_3 for sale
SCDEM	Total impure CO_2 emissions from the superstructure
S59	Urea for sale
S423	Methanol for sale

Table 4-109 Stream Relationship for Mass Balance in the Superstructure

Relationship	Description
$F_2 + F_3 = F_4$	Sulfur from Frasch mines/wells and Claus recovery to sulfuric acid plant
$F_5 = F_7 + F_8 + F_9 + F_{200} + F_{402} + F_{410}$	Air to sulfuric acid, nitric acid, ammonia, electric furnace, SO_2 recovery, and S and SO_2 recovery plant
$F_6 = F_{10} + F_{11} + F_{300} + F_{83} + F_{701} + F_{924}$	Natural gas to ammonia, methanol, power plant, acetic acid, new acetic acid plant, and other CO_2 consuming plants
$F_{16} + F_{18} = F_{24} + F_{27} + F_{28} + F_{apply}$	LP steam from sulfuric acid and power plant to phosphoric acid, urea and other plants as heat input
$F_{19} = F_{29} + F_{30} + F_{31} + F_{42} + F_{948}$	Ammonia from ammonia plant to nitric acid, ammonium nitrate, ammonium phosphate, urea plant, for sale, and methylamines plant
$F_{20} = F_{32} + F_{33} + F_{64} + F_{82} + F_{700} + F_{922}$	CO_2 from ammonia plant to urea, methanol, acetic acid, emission to atmosphere, new acetic acid, and other CO_2 consuming processes
$F_{30} = F_{43} + F_{44}$	Ammonia to ammonium phosphate plant and for sale
$F_{46} = F_{54} + F_{59}$	Urea from urea plant to UAN plant and for sale
$F_{60} = F_{39} + F_{40} + F_{41}$	Phosphoric acid from phosphoric acid plant to GTSP, ammonium phosphate plant and for sale
$F_{47} + F_{991} = F_{423} + F_{424}$	Methanol from methanol plant and other methanol production plants to acetic acid plant and for sale
$F_{1069} = F_{1070} + F_{1071} + F_{971}$	Ethylbenzene from ethylbenzene plant to styrene plant, for sale, and new styrene process

Table 4-109 Continued

Relationship	Description
$F_{CDEM} = F_{301} + F_{801}$ $+ F_{81}^{(CO_2)} + F_{15}^{(CO_2)} + F_{802}^{(CO_2)}$ $+ F_{166} + F_{151}^{(CO_2)} + F_{403}^{(CO_2)}$ $+ F_{413}^{(CO_2)} + F_{949}^{(CO_2)}$	Impure CO_2 emissions from power plant, urea, nitric acid, sulfuric acid, methanol, electric furnace, SO_2 recovery, S and SO_2 recovery, and methylamines plants
$F_{22} = F_{408} + F_{400} + F_{416}$	Gypsum from wet process for phosphoric acid to electric furnace and Haifa processes, and to the gypsum stack
$F_{112} = F_{114} + F_{115}$	Phosphoric acid from electric furnace to GTSP, MAP and DAP plants
$F_{87} = F_{117} + F_{118}$	Phosphoric acid from Haifa process to GTSP, MAP and DAP plants
$F_{922} = F_{912} + F_{935} + F_{942}$ $+ F_{946} + F_{953} + F_{958} + F_{963}$ $+ F_{967} + F_{972} + F_{980} + F_{984}$ $+ F_{993}$	CO_2 from ammonia plant to new CO_2 consuming processes, such as propane degydrogenation with CO_2, H_2, formic acid, methylamines, methanol (Jun), methanol (Bonivardi), methanol (Nerlov), methanol (Ushikoshi), new styrene, ethanol, DME, and graphite processes
$F_{924} = F_{934} + F_{992}$	Natural gas to new processes, such as graphite and H_2
$F_{936} + F_{918} + F_{916} + F_{994} =$ $F_{903} + F_{943} + F_{947} + F_{981}$ $+ F_{985} + F_{954} + F_{959} + F_{964}$ $+ F_{968}$	H_2 produced from H_2, propane dehydrogenation, propane dehydrogenation with CO_2 and graphite processes to for sales, formic acid, methylamines, ethanol, DME, methanol (Jun), methanol (Bonivardi), methanol (Nerlov), and methanol (Ushikoshi) processes
$F_{955} + F_{961} + F_{965}$ $+ F_{969} = F_{991}$	Methanol produced from methanol (Jun), methanol (Bonivardi), methanol (Nerlov), and methanol (Ushikoshi) processes

Table 4-110 Stream Relationship for Energy Balance in the Superstructure

Relationship	Description
Tlp = Ts24	LP from sulfuric acid plant ($S16_S$) and LP to phosphoric acid plant ($S24_S$) have same temperature.
Tlp = Tlpp	LP from sulfuric acid plant (SS16) and LP from power plant ($S18_S$) have same temperature.
TO2b = TO2a	Air to nitric acid plant (S8) and air to ammonia plant (S9) have same temperature.
TNH3a = TNH3b	NH_3 from NH_3 plant (S19) and NH_3 to nitric acid plant (S29) have same temperature.
TNH3a = TNH3i	NH_3 from NH_3 plant (S19) and NH_3 to urea plant (S31) have same temperature.

Table 4-110 Continued

Relationship	Description
TNH3a = TNH3k	NH_3 from NH_3 plant (S19) and NH_3 to MAP and DAP plant (S42) have same temperature.
TNH3a = TNH3j	NH_3 from NH_3 plant (S19) and NH_3 to ammonium nitrate plant (S29) have same temperature.
TCO2c = TCO2i	CO_2 from NH_3 plant (S20) and CO_2 to urea plant (S32) have same temperature.
TCO2c = TCO2h	CO_2 from NH_3 plant (S20) and CO_2 to methanol plant (S33) have same temperature.
Taq = Ta	Nitric acid from nitric acid plant (S45) and nitric acid to ammonium nitrate plant (S45) have same temperature.
TCH4a = TCH4h	CH_4 to NH_3 plant (S10) and CH_4 to methanol plant (S11) have same temperature.
Thp39 = Thp40	Phosphoric acid to GTSP plant (S39) and phosphoric acid to MAP and DAP plant (S40) have same temperature.
TCO2c = Ts82	CO_2 from NH_3 plant (S20) and CO_2 to acetic acid plant (S82) have same temperature.
TCH4a = Ts83	CH_4 to NH_3 plant (S10) and CH_4 to acetic acid plant (S83) have same temperature.
Tmet = Ts424	Methanol from methanol plant (S47) and methanol to acetic acid plant (S424) have same temperature.
T('1069') = T('1071')	Ethylbenzene from ethylbenzene plant (S1069) and ethylbenzene to styrene plant (S1071) have same temperature.
TO2a = Ts402	Air to ammonia plant (S9) and air to SO_2 recovery plant have same temperature.
TO2a = Ts410	Air to ammonia plant (S9) and air to S and SO_2 recovery plant (S410) have same temperature.
TO2a = Ts200	Air to ammonia plant (S9) and air to electric furnace plant (S200) have same temperature.
Thp39 = Thp112	Phosphoric acid from wet process to GTSP plant (S39) and phosphoric acid from electric furnace plant (S112) have same temperature.
Thp39 = Ts87	Phosphoric acid from wet process to GTSP plant (S39) and phosphoric acid from Haifa process (S87) have same temperature.
Ts22 = Ts400	Gypsum from wet process (S22) and gypsum to SO_2 recovery plant (S400) have same temperature.
Ts22 = Ts408	Gypsum from wet process (S22) and gypsum to S and SO_2 recovery plant (S408) have same temperature.
TCH4a = Ts701	CH_4 to NH_3 plant (S10) and CH_4 to new acetic acid plant (S701) have same temperature.

Table 4-110 Continued

Relationship	Description
TCO2c = Ts700	CO_2 from NH_3 plant (S20) and CO_2 to new acetic acid plant (S700) have same temperature.
TCH4a = T('924')	CH_4 to NH_3 plant (S10) and CH_4 to new processes added in the superstructure (S924) have same temperature.
TCO2c = T('922')	CO_2 from NH_3 plant (S20) and CO_2 to new CO2 consuming processes (S922) have same temperature.
TNH3a = T('948')	NH_3 from NH_3 plant (S19) and NH_3 to methylamines plant (S948) have same temperature.
Ts424 = T('991')	Methanol from methanol plant (S47) and methanol from the new methanol processes (S991) have same temperature.
T('994') = T('959')	H_2 from graphite plant (S994) and H_2 to methanol (Bonivardi) plant (S959) have same temperature.
T('912') = T('953')	CO_2 to propane dehydrogenation with CO_2 plant (S912) and CO_2 to methanol (Jun) plant (S953) have same temperature.
T('994') = T('918')	H_2 from graphite plant (S994) and H_2 from propane dehydrogenation plant (S918) have same temperature.
T('994') = T('916')	H_2 from graphite plant (S994) and H_2 from propane dehydrogenation with CO_2 plant (S916) have same temperature.
T('994') = T('903')	H_2 from graphite plant (S994) and H_2 for sale (S903) have same temperature.
T('994') = T('943')	H_2 from graphite plant (S994) and H_2 to formic acid plant (S943) have same temperature.
T('912') = T('935')	CO_2 to propane dehydrogenation with CO_2 plant (S912) and CO_2 to H_2 plant (S935) have same temperature.
T('994') = T('981')	H_2 from graphite plant (S994) and H_2 to ethanol plant (S981) have same temperature.
T('994') = T('985')	H_2 from graphite plant (S994) and H_2 to DME plant (S985) have same temperature.
T('912') = T('942')	CO_2 to propane dehydrogenation with CO_2 plant (S912) and CO_2 to formic acid plant (S942) have same temperature.
T('912') = T('972')	CO_2 to propane dehydrogenation with CO_2 plant (S912) and CO_2 to new styrene plant (S972) have same temperature.
T('994') = T('947')	H_2 from graphite plant (S994) and H_2 to methylamines plant (S947) have same temperature.
T('994') = T('968')	H_2 from graphite plant (S994) and H_2 to methanol (Ushikoshi) plant (S968) have same temperature.

Table 4-110 Continued

Relationship	Description
T('994') = T('964')	H_2 from graphite plant (S994) and H_2 to methanol (Nerlov) plant (S964) have same temperature.
T('994') = T('954')	H_2 from graphite plant (S994) and H_2 to methanol (Jun) plant (S954) have same temperature.
T('912') = T('967')	CO_2 to propane dehydrogenation with CO_2 plant (S912) and CO_2 to methanol (Ushikoshi) plant (S967) have same temperature.
T('912') = T('963')	CO_2 to propane dehydrogenation with CO_2 plant (S912) and CO_2 to methanol (Nerlov) plant (S963) have same temperature.
T('924') = T('934')	CH_4 to the new processes added in the superstructure (S924) and CH_4 to H_2 plant (S992) have same temperature.
T('912') = T('958')	CO_2 to propane dehydrogenation with CO_2 plant (S912) and CO_2 to methanol (Bonivardi) plant (S958) have same temperature.
T('912') = T('946')	CO_2 to propane dehydrogenation with CO_2 plant (S912) and CO_2 to methylamines plant (S946) have same temperature.
T('924') = T('992')	CH_4 to the new processes added in the superstructure (S924) and CH_4 to graphite plant (S992) have same temperature.
T('912') = T('980')	CO_2 to propane dehydrogenation with CO_2 plant (S912) and CO_2 to ethanol plant (S980) have same temperature.
T('912') = T('984')	CO_2 to propane dehydrogenation with CO_2 plant (S912) and CO_2 to DME plant (S984) have same temperature.
T('912') = T('993')	CO_2 to propane dehydrogenation with CO_2 plant (S912) and CO_2 to graphite plant (S993) have same temperature.
T('1069') = T('971')	Ethylbenzene from ethylbenzene plant (S1069) and ethylbenzene to new styrene plant (S971) have same temperature.
T('912') = T('922')	CO_2 to propane dehydrogenation with CO_2 plant (S912) and CO_2 from ammonia plant to CO_2 consuming processes (S992) have same temperature.
T('991') = T('965')	Methanol from the new methanol processes (S991) and methanol from methanol (Nerlov) plant (S965) and have same temperature.
T('991') = T('955')	Methanol from the new methanol processes (S991) and methanol from methanol (Jun) plant (S955) and have same temperature.

Table 4-110 Continued

Relationship	Description
T(‘991’) = T(‘961’)	Methanol from the new methanol processes (S991) and methanol from methanol (Bonivardi) plant (S965) and have same temperature.
T(‘991’) = T(‘969’)	Methanol from the new methanol processes (S991) and methanol from methanol (Ushikoshi) plant (S969) and have same temperature.

The model of the superstructure of chemical production complex is a mixed integer nonlinear programming problem. For mixed integer optimization, binary variables are associated with the production capacities of each plant. If the binary variable for a process is one, then the plant operates at least at its lower bound on the production capacity. If the binary variable of a process is zero, then the production capacity of that process is zero, and the plant is not in the optimal structure. Relations among the binary variables and the logic constraints used in the System are given in Table 4-111, and the binary variables associated the plants are:

acetic acid (Y_{11})
acetic acid-new process (Y_{12})
SO_2 recovery from gypsum (Y_{13})
S and SO_2 recovery from gypsum (Y_{14})
phosphoric acid, electric furnace (Y_1)
phosphoric acid, Haifa process (Y_2)
phosphoric acid, wet process (Y_3)
methanol (Y_{16})
methanol – Jun, et al., 1998 (Y_{31})
methanol - Bonivardi, et al., 1998 (Y_{32})
methanol – Nerlov and Chorkendorff, 1999 (Y_{33})
methanol – Ushikoshi, et al., 1998 (Y_{34})
styrene-new process (Y_{35})
styrene (Y_{40})
ethyl benzene (Y_{41})
formic acid (Y_{29})

methylamines (Y_{30}) ethanol (Y_{37})

dimethyl ether (Y_{38}) propylene from CO_2 (Y_{23})

propylene from propane dehydrogenation (Y_{24})

synthesis gas (Y_{27}) graphite (Y_{39})

Table 4-111 Logical Relations Used to Select the Optimal Structure

Logic Expression	Logic Meaning
$Y_{11} + Y_{12} \leq 1$	At most one of these two acetic acid plants is selected.
$Y_{13} + Y_{14} \leq Y_3$	At most one of these two S and SO_2 recovery plants is selected only if phosphoric acid (wet process) is selected.
$Y_{16} + Y_{31} + Y_{32} + Y_{33} + Y_{34} \leq 1$	At most one of the five methanol plants is selected, the existing one or one of the four proposed plants.
$Y_{11} \leq Y_{16} + Y_{31} + Y_{32} + Y_{33} + Y_{34}$	Only if at least one of these five methanol plants is selected, the conventional acetic acid may be selected.
$Y_{35} + Y_{40} \leq Y_{41}$	At most one of these two styrene plants is selected only if ethylbenzene plant is selected.
$Y_{29} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of the four plants that produce H_2 is selected, the formic acid plant may be selected.
$Y_{30} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of the four plants that produce H_2 is selected, the methylamines plant may be selected.
$Y_{31} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of the four plants that produce H_2 is selected, the new methanol plant may be selected.
$Y_{32} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of the four plants that produce H_2 is selected, the new methanol plant may be selected.
$Y_{33} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of the four plants that produce H_2 is selected, the new methanol plant may be selected.
$Y_{34} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of the four plants that produce H_2 is selected, the new methanol plant may be selected.
$Y_{37} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of the four plants that produce H_2 is selected, the ethanol plant may be selected.
$Y_{38} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of the four plants that produce H_2 is selected, the dimethyl ether plant may be selected.

Referring to Table 4-111, the conventional processes and the corresponding potentially new processes were compared to each other for acetic acid, S and SO_2 recovery, methanol and styrene; and the best processes were selected. Also, hydrogen must be available for plants that require hydrogen for them to be included in the complex.

For optimization, upper and lower bounds of the production capacities of plants in the complex are required. The upper bounds for the potentially new processes were from the HYSYS simulations that were based on actual plants. For convenience, the lower bound for the production capacity was selected as half the value of upper bound. If a process is selected, it has to operate at least at the lower bound of its production capacity. The upper bounds and lower bounds of the production capacities of all the plants in the chemical complex are shown in Table 4-112.

Table 4-112 Plant Capacities of the Chemical Production Complex

Plant Names	Capacity Constraints (metric tons per year)
Ammonia	$329{,}000 \le F_{19} \le 658{,}000$
Nitric acid	$89{,}000 \le F_{45}^{(HNO_3)} \le 178{,}000$
Ammonium nitrate	$113{,}000 \le F_{56} + F_{62}^{(AN)} \le 227{,}000$
Urea	$49{,}900 \le F_{46} + F_{53}^{(UREA)} \le 99{,}800$
Methanol	$91{,}000 \le F_{47} \le 181{,}000$
UAN	$30{,}000 \le F_{58} \le 60{,}000$
MAP	$146{,}000 \le F_{52} \le 293{,}000$
DAP	$939{,}000 \le F_{57} \le 1{,}880{,}000$
GTSP	$374{,}000 \le F_{51} \le 749{,}000$
Contact process sulfuric acid	$1{,}810{,}000 \le F_{14}^{(H_2SO_4)} \le 3{,}620{,}000$
Wet process phosphoric acid	$635{,}000 \le F_{60}^{(P_2O_5)} \le 1{,}270{,}000$
Electric furnace phosphoric acid	$635{,}000 \le F_{112}^{(P_2O_5)} \le 1{,}270{,}000$
Haifa phosphoric acid	$635{,}000 \le F_{87}^{(P_2O_5)} \le 1{,}270{,}000$
Acetic acid (conventional)	$4{,}080 \le F_{84} \le 8{,}160$
Acetic acid (new)	$4{,}090 \le F_{702} \le 8{,}180$
SO_2 recovery from gypsum	$987{,}000 \le F_{405} \le 1{,}970{,}000$

Table 4-112 Continued

Plant Names	Capacity Constraints (metric tons per year)
S and SO_2 recovery from gypsum	$494{,}000 \le \frac{32.06}{64.06} F_{411} + F_{412} \le 988{,}000$
Ethylbenzene	$431{,}000 \le F_{1069} \le 862{,}000$
Styrene	$386{,}000 \le F_{1072} \le 771{,}000$
New Styrene	$181{,}000 \le F_{974} \le 362{,}000$
New Methanol (Bonivardi)	$240{,}000 \le F_{961} \le 480{,}000$
New Methanol (Jun)	$240{,}000 \le F_{955} \le 480{,}000$
New Methanol (Nerlov)	$240{,}000 \le F_{965} \le 480{,}000$
New Methanol (Ushikoshi)	$240{,}000 \le F_{969} \le 480{,}000$
New Formic Acid	$39{,}000 \le F_{944} \le 78{,}000$
New Methylamines	$13{,}200 \le F_{950} \le 26{,}400$
New Ethanol	$52{,}000 \le F_{982} \le 104{,}000$
New DiMethyl Ether (DME)	$22{,}900 \le F_{987} \le 45{,}800$
New Graphite	$23{,}000 \le F_{995} \le 46{,}000$
New Hydrogen	$6{,}700 \le F_{936} \le 13{,}400$
New Propylene by CO_2	$21{,}000 \le F_{914} \le 41{,}900$
New Propylene	$20{,}900 \le F_{919} \le 41{,}800$

D. Processes Used in Other Studies with the Chemical Production Complex

The processes described in this section were used in other studies with the chemical production complex in the Chemical Complex Analysis System.

D-1. Potassium Chloride (Austin, 1984)

In the chemical complex there are three options for potassium chloride, i.e., Trona process, IMC process, and Sylvinite process. The detailed description for these processes is given below.

Since there was no available potassium chloride production capacity in the lower Mississippi River corridor, a tyical capacity of 5,600,000 metric tons per year of potassium chloride was used for all these three processes.

D-1-1. KCl Manufacture by Trona Process (Austin, 1984)

D-1-1-1. Process Description

The lake brine with the specific composition (Table 4-113) is pumped and concentrated first to get three branches of output streams. One is the water evaporated; one is the input to the soda products plant with additional sulfuric acid to produce Na_2SO_4, Na_2CO_3, H_3PO_4, etc; the other is the input to the potash plant to produce KCl and then to borax plant which is not considered in this complex (Austin, 1984). The block diagram is shown in Figure 4.37 with the stream definitions in Table 4-114.

Table 4-113 Parameters in Trona Process, from Austin (1984)

Name	Meaning		Value
	Content of brine (weight fraction):		
		KCl	3.92%
		NaCl	16.25%
		Na_2SO_4	6.98%
		Na_2CO_3	5.5%
		Na_3PO_4	0.155%
		H_2O	67.195%
CONCPTR	P_2O_5 weight fraction of H_3PO_4		0.30

D-1-1-2. Material Balance and Energy Balance

Using the parameters in Table 4-113 the material balance and energy balance of Trona plant are given in Table 4-115.

In Table 4-115, the overall material balance for the whole process is given first. For the species material balance, the first equation is for the KCl balance; the second one is for the NaCl balance; the third on is for the Na_2CO_3 balance; the fourth one is for the P_2O_5 balance; the fifth one is for the H_2SO_4 balance; the sixth one is for the Na_2SO_4 balance; the seventh one is for the H_2O vapor balance; and the last one is for the overall H_2O balance.

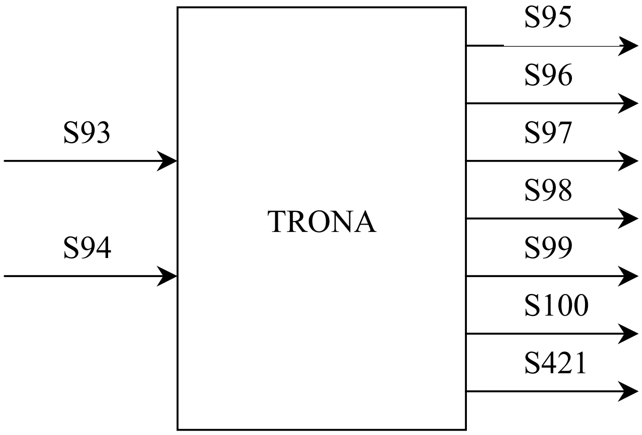


Figure 4-37 Block Diagram of Trona Plant

Table 4-114 Description of Process Streams in Trona Plant

Name of Streams	Description
Input Streams	
S93	Brine to Trona plant
S94	Contact process H_2SO_4 to Trona plant
Output Streams	
S95	Production of KCl from Trona plant
S96	Production of H_3PO_4 from Trona plant
S97	Production of NaCl from Trona plant
S98	Production of Na_2CO_3 from Trona plant
S99	Production of Na_2SO_4 from Trona plant
S100	Production of one branch of water from Trona plant
S421	Water evaporated from Trona plant

In the overall energy balance, Q_{TR} is heat input of the Trona process in the form of steam in heat exchanger for product separation, which is calculated from the energy balance. No heat loss is considered in the process. In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

Table 4-115 Constraint Equations for Trona Process

Material Balance	
Overall	$(F_{93}+F_{94})-(F_{95}+F_{96}+F_{97}+F_{98}+F_{99}+F_{100}+F_{421})=0$ where $F_{94}=F_{94}^{(H_2SO_4)}+F_{94}^{(H_2O)}$ $F_{96}=F_{96}^{(P_2O_5)}+F_{96}^{(H_2O)}$
Species	KCl: $0.0392F_{93}-F_{95}=0$ NaCl: $0.1625F_{93}-F_{97}=0$ Na_2CO_3: $0.055F_{93}-F_{98}=0$ P_2O_5: $\frac{0.00155}{163.94}F_{93}-\frac{2}{141.94}F_{96}^{(P_2O_5)}=0$ H_2SO_4: $\frac{1}{(98.08)(3)}F_{94}^{(H_2SO_4)}-\frac{1}{141.94}F_{96}^{(P_2O_5)}=0$ Na_2SO_4: $\frac{(0.155)(3)}{(100)(163.94)(2)}F_{93}+\frac{0.0698}{142.04}F_{93}-\frac{1}{142.04}F_{99}=0$ Vapor: $F_{421}-0.24F_{93}=0$ H_2O: $((0.67195+\frac{(0.00155)(1.5)(18.02)}{163.94})F_{93}+F_{94}^{(H_2O)})-(F_{96}^{(H_2O)}-\frac{(3)(18.02)}{141.94}F_{96}^{(P_2O_5)}+F_{100}+F_{421})=0$
Energy Balance	
Overall	$(F_{95}^{(KCl)}/M^{(KCl)}H_{95}^{(KCl)}+F_{97}^{(NaCl)}/M^{(NaCl)}H_{97}^{(NaCl)}+F_{98}^{(Na_2CO_3)}/M^{(Na_2CO_3)}H_{98}^{(Na_2CO_3)}$ $+F_{99}^{(Na_2SO_4)}/M^{(Na_2SO_4)}H_{99}^{(Na_2SO_4)}+F_{100}^{(H_2O)}/M^{(H_2O)}H_{100}^{(H_2O)}$ $+F_{421}^{(H_2O)}/M^{(H_2O)}H_{421}^{(H_2O)}+\Sigma F_{96}^{(i)}/M^{(i)}H_{96}^{(i)})-(\Sigma F_{93}^{(j)}/M^{(j)}H_{93}^{(j)}$ $+\Sigma F_{94}^{(k)}/M^{(k)}H_{94}^{(k)})-Q_{TR}=0$ where i = H_2O, P_2O_5; j = KCl, NaCl, Na_2CO_3, $Na_3(PO_4)_2$, Na_2SO_4, H_2O; k = H_2O, H_2SO_4
Enthalpy Function	$H_k^i(T)=(a_1^i+\frac{1}{2}a_2^iT+\frac{1}{3}a_3^iT^2+\frac{1}{4}a_4^iT^3+\frac{1}{5}a_5^iT^4+\frac{b_1^i}{T})RT$ J/mol i = KCl, NaCl, H_2O, H_2SO_4; k = 93, 94, 95, 96, 97, 100, 421

Table 4-115 Continued

Energy Balance (Continued)		
Enthalpy Function	$H_k^{(Na_3PO_4)}(T) = ((-458.27)(1000) + (36.68)(T - 298.15))(4.182)$ k=93 Source: Lide (1982)	J/mol
	$H_k^{(Na_2CO_3)}(T) = ((-270.24)(1000) + (26.84)(T - 298.15))(4.182)$ k=93, 98 Source: Lide (1982)	J/mol
	$H_k^{(Na_2SO_4)}(T) = ((-331.52)(1000) + (30.64)(T - 298.15))(4.182)$ k=93, 99 Source: Lide (1982)	J/mol
	$H_k^{(P_2O_5)} = (-1278.437)(1000) + (106.014)(T - 298.15) J/mol$ k=96 Source: Lide (1982)	J/mol

In the material balance part, there are 13 variables and 13 equations including the dependent overall mass balance, so the number of degrees of freedom is 1. For the material and energy balance, there are 39 variables and 30 equations including the dependent overall mass balance, so the number of degrees of freedom is 10.

D-1-2. KCl Manufacture by IMC Process (Austin, 1984)

D-1-2-1. Process Description

In the International Minerals and Chemical Corporation (IMC), process feed is the ore that is sylvinite ($xNaCl{\cdot}KCl$) and carnallite ($KCl{\cdot}MgCl_2{\cdot}6H_2O$). This ore is treated first to leach out the carnallite, deslime and separate the potassium salts into fines and coarse materials. After this separation the fines are deslimed by a hydroseparator and combined with the coarse salts. Both the fines and the coarse salts are conducted to flotation cells to separate the potassium salts from the sodium chloride by flotation (Austin, 1984). The block diagram is given in Figure 4.38 with the stream definitions in Table 4-116.

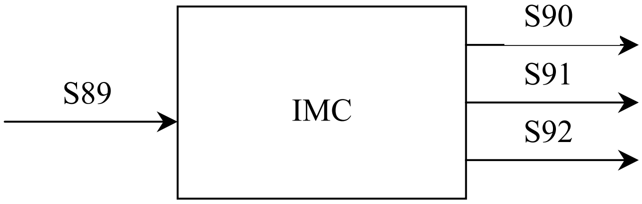


Figure 4.38 Block Diagram of IMC Plant

Table 4-116 Description of Process Streams in IMC Plant

Name of Streams	Description
Input Streams	
S89	Ore to IMC plant
Output Streams	
S90	Production of KCl from IMC plant
S91	Production of NaCl from IMC plant
S92	Production of other materials ($MgCl_2$ and H_2O) from IMC plant

D-1-2-2. Material Balance and Energy Balance

Using the parameters in Table 4-117 the material balance and energy balance of the IMC plant are given in Table 4-118.

In Table 4-118, the overall material balance for the whole process is given first. For the species material balance, the first equation is for the KCl balance; and the second one is for the NaCl balance.

In the overall energy balance, Q_{IM} is heat input of the IMC process in the form of steam in dryer for product separation, which is calculated from the energy balance. Q_{out} is the heat loss during the unit operations in the IMC process based on the unit of KCl product, 1.7 MJ per lb of KCl (Austin, 1984). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 4 variables and 3 equations, so the number of degrees of freedom is 1. For the material and energy balance, there are 14 variables and 9 equations including the dependent overall mass balance, so the number of degrees of freedom is 5.

Table 4-117 Parameters in IMC Plant, from Austin (1984)

Parameters		
Ore composition (weight fraction):		
	KCl	15.92%
	NaCl	62.38%
	Others	21.70%

Table 4-118 Constraint Equations for IMC Plant

Material Balance	
Overall	$F_{89} - (F_{90} + F_{91} + F_{92}) = 0$
Species	KCl: $0.1592F_{89} - F_{90} = 0$
	NaCl: $0.6238F_{89} - F_{91} = 0$
Energy Balance	
Overall	$(F_{90}^{(KCl)} / M^{(KCl)} H_{90}^{(KCl)} + F_{91}^{(NaCl)} / M^{(NaCl)} H_{91}^{(NaCl)} + \Sigma F_{92}^{(i)} / M^{(i)} H_{92}^{(i)}) -$ $F_{89}^{(ORE)} / M^{(ORE)} H_{89}^{(ORE)} + Q_{loss} F_{90}^{(KCl)} - Q_{IM} = 0$ where i = $MgCl_2$, H_2O
Enthalpy Function	$H_k^i(T) = (a_1^i + \frac{1}{2}a_2^i T + \frac{1}{3}a_3^i T^2 + \frac{1}{4}a_4^i T^3 + \frac{1}{5}a_5^i T^4 + \frac{b_1^i}{T})RT$ J/mol i = KCl, NaCl, $MgCl_2$, H_2O; k = 90, 91, 92 $H_k^{(ORE)}(T) = 10H_k^{(NaCl)}(T) + 2H_k^{(KCl)}(T) + H_k^{(MgCl_2)}(T) + 6H_k^{(H_2O)}(T)$ J/mol k=89

D-1-3. KCl Manufacture by Sylvinite Process (Austin, 1984)

D-1-3-1. Process Description

The raw material is sylvinite from a mine. The process depends primarily on the fact that sodium chloride is less soluble in a hot than in a cold saturated solution of potassium chloride. Thus, when a saturated solution of the mixed salts in water is cooled from its boiling point, potassium chloride separates out, contaminated with only the sodium chloride that is entrained. Then potassium chloride can be obtained by additional treatment and separation (Austin, 1984). The block diagram is shown in Figure 4.39 with the stream definitions in Table 4-119.

Figure 4.39 Block Diagram of Sylvinite Process

Table 4-119 Description of Process Streams in Sylvinite Process

Name of Streams	Description
Input Streams	
S101	Raw material - sylvinite to Sylvinite process
Output Streams	
S102	Production of KCl from Sylvinite process
S103	Production of NaCl from Sylvinite process
S104	Production of other materials from Sylvinite process

D-1-3-2. Material Balance and Energy Balance

Using the parameters in Table 4-120 the material balance and energy balance of KCl manufactured from Sylvinite process are given in Table 4-121.

In Table 4-121, the overall material balance for the whole process is given first. For the species material balance, the first equation is for the KCl balance; and the second one is for the NaCl balance.

In the overall energy balance, Q_{SY} is heat input in the form of steam in heat exchanger and heater for product separation in the Sylvinite process, which is calculated from the energy balance. Q_{out} is the heat output removed by cooling water in heat exchanger and condenser in the Sylvinite process based on the unit of KCl product, 1.5 MJ per lb of KCl (Austin, 1984). In enthalpy functions, the coefficients a_1, a_2, a_3, a_4, a_5, and b_1 for different species are given in Table A-1 in Appendix A.

In the material balance part, there are 4 variables and 3 equations, so the number of degrees of freedom is 1. For the material and energy balance, there are 15 variables and 10 equations, so the number of degrees of freedom is 5.

Table 4-120 Parameters in Producing KCl from Sylvinite Process, from Austin (1984)

Parameters		
Sylvinite composition(weight fraction):		
	KCl	42.7%
	NaCl	56.6%

Table 4-121 Constraint Equations for Producing KCl from Sylvinite Process

Material Balance	
Overall	$F_{101} - (F_{102} + F_{103} + F_{104}) = 0$
Species	KCl: $0.427F_{101} - F_{102} = 0$
	NaCl: $0.566F_{101} - F_{103} = 0$
Energy Balance	
Overall	$(F_{102}^{(KCl)} / M^{(KCl)} H_{102}^{(KCl)} + F_{103}^{(NaCl)} / M^{(NaCl)} H_{103}^{(NaCl)}$ $+ F_{104}^{(OTHER)} / M^{(OTHER)} H_{104}^{(OTHER)}) - \Sigma F_{101}^{(i)} / M^{(i)} H_{101}^{(i)} + Q_{loss} F_{102} - Q_{SY} = 0$ where i = KCl, NaCl, OTHER (Assume other material has same molecular weight and enthalpy as KCl)
Enthalpy Function	$H_k^i(T) = (a_1^i + \frac{1}{2}a_2^i T + \frac{1}{3}a_3^i T^2 + \frac{1}{4}a_4^i T^3 + \frac{1}{5}a_5^i T^4 + b_1^i)RT$ J/mol i = KCl, NaCl, OTHER k = 101, 102, 103

D-2. Solid Fertilizer

Since there was no available solid fertilizer production capacity in the lower Mississippi River corridor, a tyical capacity of 10,000 metric tons per year of solid fertilizer as lower bound was used.

D-2-1. Process Description

The solid fertilizer can be produced by simply blending several intermediates in the chemical production complex. Its composition can be changed according to the specific market application. The block diagram is shown in Figure 4.40 with the stream definitions in Table 4-122.

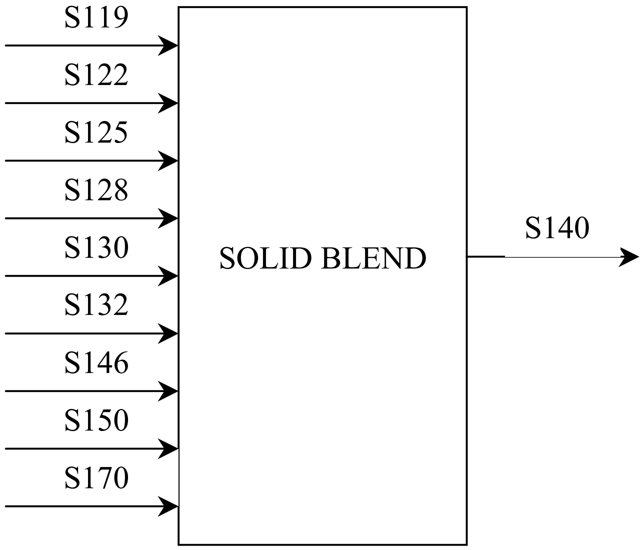


Figure 4.40 Block Diagram of Solid Blend Plant

D-2-2. Material Balance and Energy Balance

Using the parameters in Table 4-123 the material balance and energy balance of the solid fertilizer plant are given in Table 4-124.

Table 4-122 Description of Process Streams in Solid Blend Plant

Name of Streams	Description
Input Streams	
S119	KCl from Trona to solid blend plant
S122	KCl from IMC to solid blend plant
S125	KCl from sylvinite to solid blend plant
S128	GTSP to solid blend plant
S130	MAP to solid blend plant
S132	DAP to solid blend plant
S146	Ammonium nitrate to solid blend plant
S150	Urea to solid blend plant
S170	Fillings to solid blend plant
Output Streams	
S140	Production of solid blend mixture

Table 4-123 Parameters in Solid Blend Plant

Name	Meaning	Value
	Solid fertilizer composition (weight fraction)	
NSF	N	0.18
PSF	P_2O_5	0.18
KSF	K_2O	0.18

Table 4-124 Constraint Equations in Solid Blend Plant

Material Balance	
Overall	$(F_{119} + F_{122} + F_{125} + F_{128} + F_{130} + F_{132} + F_{146} + F_{150} + F_{170}) - F_{140} = 0$
Species	N: $\frac{NMAP}{100} F_{130} + \frac{NDAP}{100} F_{132} + \frac{(2)(14.01)}{80.06} F_{146} + \frac{(2)(14.01)}{60.07} F_{150} - (NSF)F_{140} = 0$ P_2O_5: $(PGTSP)F_{128} + \frac{P2O5MAP}{100} F_{130} + \frac{P2O5DAP}{100} F_{132} - (PSF)F_{140} = 0$ K_2O: $\frac{94.2}{(2)(74.55)} (F_{119} + F_{122} + F_{125}) - (KSF)F_{140} = 0$

In Table 4-124, the overall material balance for the whole process is followed by the species material balance. The first equation is for the N balance; the second one is for the P_2O_5 balance; the last one is for the K_2O balance.

In the material balance part, there are 11 variables and 4 equations, so the number of degrees of freedom is 7. There is no significant energy change in this simple blending process and an energy balance is not required. Hence, for the material and energy balance, there are 11 variables and 4 equations, so the number of degrees of freedom is 7.

D-3. Liquid Fertilizer

Since there was no available liquid fertilizer production capacity in the lower Mississippi River corridor, a tyical capacity of 10,000 metric tons per year of liquid fertilizer as lower bound was used.

D-3-1. Process Description

The liquid fertilizer can be produced by simply blending several intermediates in the chemical production complex. Its composition can be changed according to the specific market application. The block diagram is shown in Figure 4.41 with the stream definitions in Table 4-125.

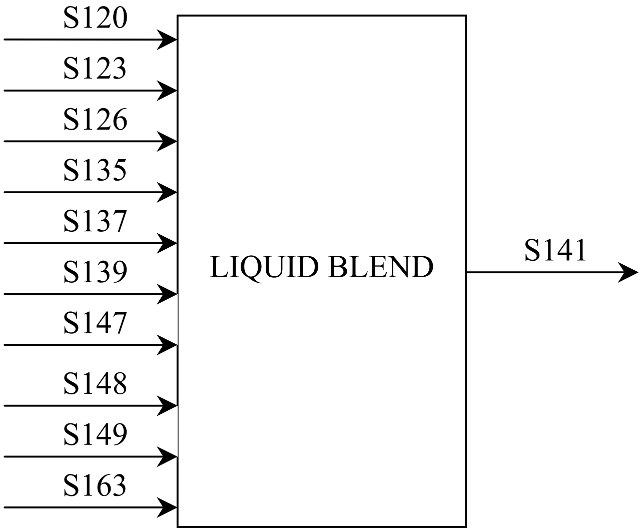


Figure 4.41 Block Diagram of Liquid Blend Plant

Table 4-125 Description of Process Streams in Liquid Blend Plant

Name of Streams	Description
Input Streams	
S120	KCl from Trona to liquid blend plant
S123	KCl from IMC to liquid blend plant
S126	KCl from Sylvinite to liquid blend plant
S135	Ammonium nitrate to liquid blend plant
S137	UAN solution to liquid blend plant
S139	Urea to liquid blend plant
S147	GTSP to liquid blend plant
S148	MAP to liquid blend plant
S149	DAP to liquid blend plant
S163	filling materials to liquid blend plant
Output Streams	
S141	Production of liquid blend mixture

D-3-2. Material Balance and Energy Balance

Using the parameters in Table 4-126 the material balance and energy balance of the liquid fertilizer plant are given in Table 4-127.

Table 4-126 Parameters in Liquid Blend Plant

Name	Meaning	Value
	Liquid fertilizer composition (weight fraction)	
NLF	N	0.09
PLF	P_2O_5	0.09
KLF	K_2O	0.06

In Table 4-127, the overall material balance for the whole process is given with the mixture stream expressions. For the species material balance, the first equation is for the N balance; the second one is for the P_2O_5 balance; the last one is for the K_2O balance.

In the material balance part, there are 14 variables and 5 equations, so the number of degrees of freedom is 9. There is no significant energy change in this simple blending process and an energy balance is not required. Hence, for the material and energy balance, there are 14 variables and 5 equations, so the number of degrees of freedom is 9.

Table 4-127 Constraint Equations in Liquid Blend Plant

Material Balance	
Overall	$(F_{120}+F_{123}+F_{126}+F_{135}+F_{137}+F_{139}+F_{147}+F_{148}+F_{149}+F_{163})-F_{141} = 0$ $F_{137} = F_{137}^{(UAN)} + F_{137}^{(H_2O)}$
Species	N: $\frac{(2)(14.01)}{80.06}F_{135} + (CONCNUAN)F_{137} + \frac{(2)(14.01)}{60.07}F_{139} + \frac{NMAP}{100}F_{148} + \frac{NDAP}{100}F_{149} - (NLF)F_{141} = 0$ P_2O_5: $(PGTSP)F_{147} + \frac{P2O5MAP}{100}F_{148} + \frac{P2O5DAP}{100}F_{149} - (PLF)F_{141} = 0$ K_2O: $\frac{94.2}{(2)(74.55)}(F_{120}+F_{123}+F_{126}) - (KLF)F_{141} = 0$

E. Validation of the Agricultural Chemical Production Complex

The industrial advisory group provided a description of the plants in the chemical production complex based on the plants in the lower Mississippi River corridor. These are shown in Figure 4.42 where the mass flow rates are in tons per day. This information in Figure 4.42 was obtained from a detailed description of these plants in an Excel workbook with seventeen worksheets. The Excel worksheets are given in Appendix C. The industrial data was used to validate the simulation of the chemical production complex, and this data used for validation are the 58 mass flow rates shown in Table 4-128.

The simulation of chemical production complex of existing plants (agricultural chemical complex) in the Chemical Complex Analysis System has to be validated using results from the industrial advisory group. The simulation has to agree with the information provided by the industrial advisors for the existing plants in the lower Mississippi River corridor. In this section, the chemical production complex in the Chemical Complex Analysis System is compared to the description of the plants in the Excel workbook. Comparing the results obtained with the System with the actual plants will serve to show that the System is an accurate representation of the actual plants.

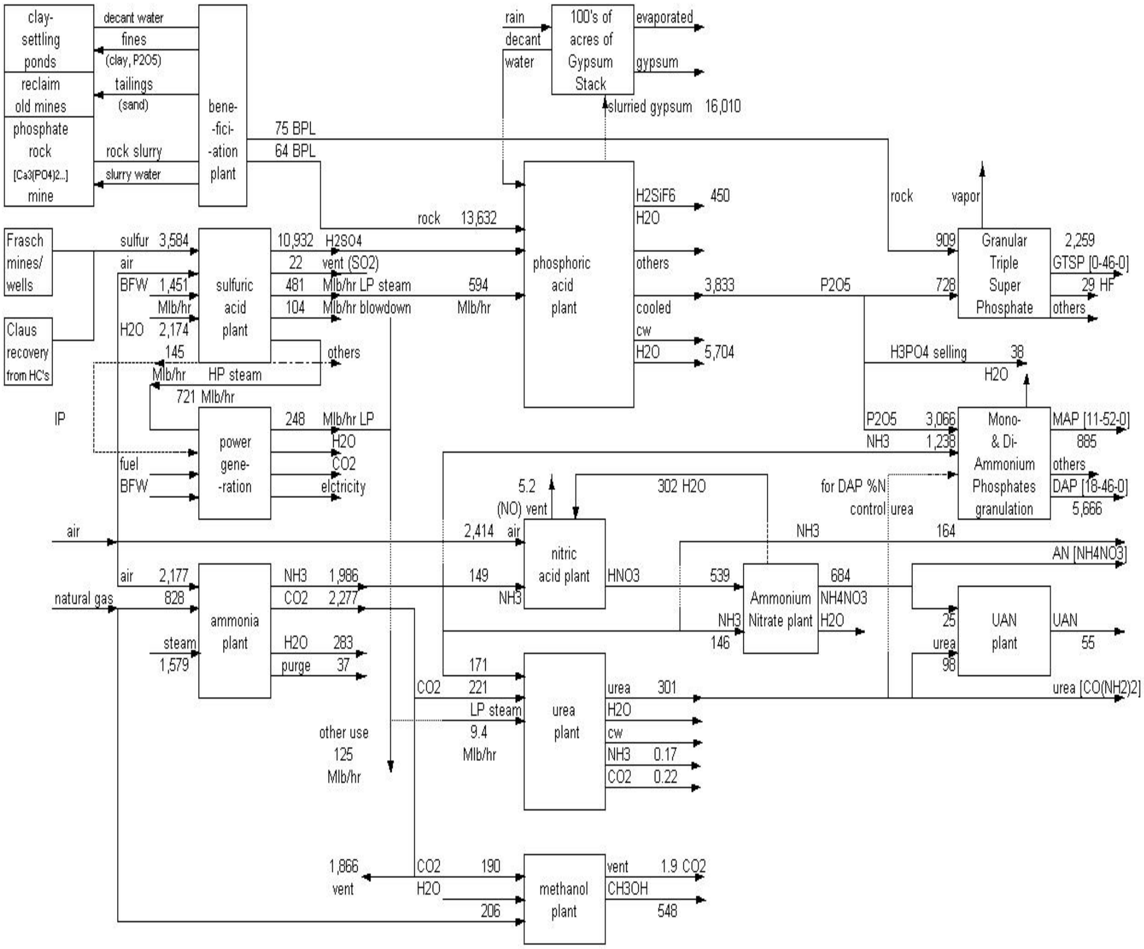


Figure 4.42 Chemical Production Complex Based on Plants in the Lower Mississippi River Corridor, from Hertwig (2004), Agricultural Chemical Complex, Flow Rates Tons Per Day (TPD) if Not Specified

In the simulation of the agricultural chemical complex in the System, there are 275 variables, and 233 linear and nonlinear equality constraints that describe material and energy balances, rate equations and equilibrium relations for the plants. Hence, the degrees of freedom for the chemical production complex = number of independent variables – number of independent constraint equations = 275-233 = 42. Consequently, 42 process variables can be specified, and all of the others are calculated from the model. However, specifying industry data will not validate the model. Other variables have to be specified and the industry data calculated. Process temperatures and pressures were selected, and there are 36 given in Table 4-129. Consequently, it was necessary to specify the six production capacities in Table 4-130. Therefore, 42 process variables are specified and the degrees of freedom for the model = 42-42 = 0. Then the variables could be computed with the simulation.

Table 4-128 The Industry Data for the Agricultural Chemical Complex, from Hertwig (2004)

Process Names	Description	Industry Data	Unit
Sulfuric acid			
F_4	Mass flow rate of sulfur in stream S4	3,584	TPD
F_{61}	Mass flow rate of boiler feed water in steam S61	17,406	TPD
F_{66}	Mass flow rate of dilution water in stream S66	2,174	TPD
$F_{14}^{(H_2SO_4)}$	Mass flow rate of 100% H_2SO_4 in stream S14	10,934	TPD
$F_{15}^{(SO_2)}$	Mass flow rate of SO_2 emission in stream S15	22	TPD
F_{16}	Mass flow rate of LP in stream S16	481	Mlb/hr
F_{17}	Mass flow rate of HP in stream S17	721	Mlb/hr
F_{77}	Mass flow rate of IP in stream S77	145	Mlb/hr
F_{67}	Mass flow rate of blow down water in stream S67	104	Mlb/hr

Table 4-128 Continued

Process Names	Description	Industry Data	Unit
Phosphoric acid			
F_{13}	Mass flow rate of phosphate rock in stream S13	13,632	TPD
$F_{14}^{(H_2SO_4)}$	Mass flow rate of 100% H_2SO_4 in stream S14	10,932	TPD
F_{24}	Mass flow rate of LP in stream S24	594	Mlb/hr
F_{22}	Mass flow rate of gypsum slurry in stream S22	16,010	TPD
F_{49}	Mass flow rate of H_2SiF_6 solution in stream S49	667	TPD
F_{420}	Mass flow rate of water evaporation in stream S420	5,704	TPD
$F_{60}^{(P_2O_5)}$	Mass flow rate of P_2O_5 in stream S60	3,833	TPD
Ammonia			
F_9	Mass flow rate of air in stream S9	2,176	TPD
F_{10}	Mass flow rate of methane in stream S10	828	TPD
F_{68}	Mass flow rate of steam in stream S68	1,579	TPD
F_{20}	Mass flow rate of CO_2 in stream S20	2,277	TPD
F_{19}	Mass flow rate of NH_3 in stream S19	1,986	TPD
F_{69}	Mass flow rate of H_2O in stream S69	283	TPD
F_{70}	Mass flow rate of purge gas in stream S70	37	TPD
Nitric acid			
F_8	Mass flow rate of air in stream S8	2,839	TPD
F_{29}	Mass flow rate of NH_3 in stream S29	149	TPD
F_{71}	Mass flow rate of H_2O in stream S71	301	TPD
$F_{45}^{(HNO_3)}$	Mass flow rate of 100%HNO_3 in stream S45	539	TPD
$F_{45}^{(H_2O)}$	Mass flow rate of H_2O in stream S45	459	TPD
$F_{81}^{(NO)}$	Mass flow rate of NO in stream S81	5.24	TPD
Urea			
F_{27}	Mass flow rate of LP in stream S27	9.4	Mlb/hr
F_{31}	Mass flow rate of NH_3 in stream S31	171	TPD
F_{32}	Mass flow rate of CO_2 in stream S32	221	TPD
$F_{53} + F_{46}$	Mass flow rate of urea in stream S53 and S46	301	TPD
F_{53H_2O}	Mass flow rate of H_2O in stream S53H2O	90	TPD

Table 4-128 Continued

Process Names	Description	Industry Data	Unit
Urea (Continued)			
F_{800}	Mass flow rate of NH_3 loss in stream S800	0.17	TPD
F_{801}	Mass flow rate of CO_2 loss in stream S801	0.22	TPD
Methanol			
F_{11}	Mass flow rate of CH_4 in stream S11	206	TPD
F_{33}	Mass flow rate of CO_2 in stream S33	190	TPD
F_{47}	Mass flow rate of methanol in stream S47	548	TPD
$F_{802}^{(H_2)}$	Mass flow rate of H_2 in stream S802	0.08	TPD
$F_{802}^{(CO_2)}$	Mass flow rate of CO_2 in stream S802	1.90	TPD
$F_{802}^{(CO)}$	Mass flow rate of CO in stream S802	0.36	TPD
GTSP			
F_{12}	Mass flow rate of phosphate rock in stream S12	909	TPD
$F_{39}^{(P_2O_5)}$	Mass flow rate of P_2O_5 in stream S39	728	TPD
F_{51}	Mass flow rate of GTSP in stream S51	2,259	TPD
F_{63}	Mass flow rate of intermediate HF in stream S63	29	TPD
MAP and DAP			
$F_{40}^{(P_2O_5)}$	Mass flow rate of P_2O_5 in stream S40	3,066	TPD
F_{42}	Mass flow rate of NH_3 in stream S42	1,356	TPD
F_{52}	Mass flow rate of MAP in stream S52	885	TPD
F_{57}	Mass flow rate of DAP in stream S57	5,666	TPD
Ammonium nitrate			
$F_{45}^{(HNO_3)}$	Mass flow rate of 100% HNO_3 in stream S45	539	TPD
F_{44}	Mass flow rate of NH_3 in stream S44	146	TPD
$F_{56} + F_{62}^{(AN)}$	Mass flow rate of ammonium nitrate in stream S56 and S62	684	TPD
F_{56}	Mass flow rate of ammonium nitrate for sale in stream S56	659	TPD
$F_{62}^{(AN)}$	Mass flow rate of ammonium nitrate to UAN in stream S62	25	TPD

Table 4-128 Continued

Process Names	Description	Industry Data	Unit
UAN			
F_{54}	Mass flow rate of urea in stream S54	36,620	TPY
F_{62}	Mass flow rate of ammonium nitrate solution in stream S62	30,072	TPY
F_{58}	Mass flow rate of UAN in stream S58	66,667	TPY
Sales			
$F_{41}^{(P_2O_5)}$	Mass flow rate of P_2O_5 for sale in stream S41	38	TPD
F_{43}	Mass flow rate of NH_3 for sale in stream S43	164	TPD

The simulation solution to the constraint equations is obtained using the optimization capability in the System. An objective function is defined as a constant, 1, and then maximizing objective = 1 generates a solution to the constraint equations. The accuracy and validity of the agricultural chemical complex simulation was examined by comparing the simulation results of the agricultural chemical complex with the industry data (Hertwig, 2004) for the chemical production complex. Solving this problem will simultaneously estimate the industry data listed in Table 4-128 and all other variables in the complex model. The estimated data should agree closely with the industry data since it is accurate and consistent.

The simulation solution from the System are compared with the industry data shown in Table 4-131. The fixed process variables as the model input are not shown in Table 4-131, such as the plant capacities in Table 4-130. It showed the percentage deviation of the model and the industry data, and the largest difference ((System results – industry data)/industry data × 100) is only 2.1% of the existing plant data. This means that the constraint equations in the complex model are precise and will

Table 4-129 Fixed Stream Conditions for the Agricultural Chemical Complex (Temperature in K, and Pressure in Psia)

Name	Description	Value
TCH4a	temperature of CH_4 to ammonia plant	298.15
TO2a	temperature of O_2 to ammonia plant	298.15
TArb	temperature of Ar vent from ammonia plant	298.15
TCO2c	temperature of CO_2 from ammonia plant	298.15
TNH3a	temperature of NH_3 produced from ammonia plant	298.15
TH2Ob	temperature of H_2O to ammonia plant	298.15
TH2Oc	temperature of H_2O produced from ammonia plant	298.15
Taq	temperature of HNO_3 solution produced from nitric acid plant	298.15
TH2Od	temperature of H_2O to nitric acid plant	298.15
TCO2e	temperature of CO_2 vent from nitric acid plant	298.15
TH2Og	temperature of H_2O in S67 from the sulfuric acid plant	298.15
Tcp	temperature of BFW from the sulfuric acid plant	298.15
Tlp	temperature of LP from the sulfuric acid plant	403.83
Tip	temperature of IP from the sulfuric acid plant	454.49
Thp	temperature of HP from the sulfuric acid plant	533.15
Ph	pressure of HP from the sulfuric acid plant	600
Tana	temperature of NH_4NO_3 granular from NH_4NO_3plant	298.15
Tanb	temperature of NH_4NO_3 solution from NH_4NO_3 plant	298.15
Ts71	temperature of H_2O from NH_4NO_3 plant	408
Ts804	temperature of H_2O evaporated from NH_4NO_3 plant	408
Tua	temperature of urea granular from urea plant	298.15
Tub	temperature of urea solutionfrom urea plant	298.15
Ts800	temperature of S800	298.15
Ts801	temperature of S801	298.15
Tmet	temperature of methanol from methanol plant	298.15
Tmlp	temperature of LP to methanol plant	298.15
Ts802	temperature of purge gases from methanol plant	298.15
TH2Ol	temperature of H_2O from ammonium phosphates plant	298.15
Tmap	temperature of MAP from ammonium phosphates plant	298.15
Tdap	temperature of DAP from ammonium phosphates plant	298.15
Tra	temperature of phosacid rock to GTSP plant	298.15
Thp39	temperature of phosacid solution to GTSP plant	298.15
Tgtsp	temperature of GTSP from GTSP plant	298.15
TH2On	temperature of H_2O from GTSP plant	422.04
Thf	temperature of HF from GTSP plant	300
Ts75	temperature of cool down LP from phosphoric acid plant	373.15

predict the performance of the complex. The industry data and results from the System are independent, and this agreement establishes the accuracy of the simulation of the chemical production complex.

Table 4-130 Fixed Production Capacities for the Agricultural Chemical Complex

Descriptions	Capacities
Ammonia capacity	$F_{19} = 1{,}986\ \text{TPD}$
Nitric acid capacity	$F_{45}^{(HNO_3)} = 539\ \text{TPD}$
Urea capacity	$F_{46} + F_{53} = 301\ \text{TPD}$
Methanol capacity	$F_{47} = 548\ \text{TPD}$
Wet process phosphoric acid capacity	$F_{60}^{(P_2O_5)} = 3{,}833\ \text{TPD}$
UAN capacity	$F_{58} = 66{,}667\ \text{TPY}$

Table 4-131 Comparison of Simulated Values and Industry Data for the Agricultural Chemical Complex

Names	Unit	Industry Data	Results from the System	Percent Difference
Sulfuric acid				
F_4	TPD	3,584	3,588	0.12
F_{61}	TPD	17,406	17,409	0.01
F_{66}	TPD	2,174	2,175	0.04
$F_{14}^{(H_2SO_4)}$	TPD	10,932	10,934	0.01
$F_{15}^{(SO_2)}$	TPD	22	22	0.02
F_{16}	Mlb/hr	481	481	0.01
F_{17}	Mlb/hr	721	721	0.01
F_{77}	Mlb/hr	145	145	0.02
F_{67}	Mlb/hr	104	104	0.01
Phosphoric acid				
F_{13}	TPD	13,632	13,633	0.01
$F_{14}^{(H_2SO_4)}$	TPD	10,932	10,934	0.01
F_{24}	Mlb/hr	594	594	0.00
F_{22}	TPD	16,010	16,013	0.02
F_{49}	TPD	667	668	0.03

Table 4-131 Continued

Names	Unit	Industry Data	Results from the System	Percent Difference
Phosphoric acid				
F_{420}	TPD	5,704	5,704	0.00
Ammonia				
F_9	TPD	2,176	2,173	-0.16
F_{10}	TPD	828	828	0.08
F_{68}	TPD	1,579	1,576	-0.12
F_{20}	TPD	2,277	2,272	-0.20
F_{69}	TPD	283	283	-0.07
F_{70}	TPD	37	37	-0.17
Nitric acid				
F_8	TPD	2,839	2,818	-0.73
F_{29}	TPD	149	149	-0.22
F_{71}	TPD	301	300	-0.53
$F_{45}^{(H_2O)}$	TPD	459	459	0.00
$F_{81}^{(NO)}$	TPD	5.24	5.24	-0.07
Urea				
F_{27}	Mlb/hr	9.4	9.4	0.01
F_{31}	TPD	171	171	0.02
F_{32}	TPD	221	221	-0.06
F_{53H_2O}	TPD	90	90	0.38
F_{800}	TPD	0.17	0.17	1.19
F_{801}	TPD	0.22	0.22	0.14
Methanol				
F_{11}	TPD	206	206	-0.07
F_{33}	TPD	190	190	-0.07
$F_{802}^{(H_2)}$	TPD	0.08	0.08	1.80
$F_{802}^{(CO_2)}$	TPD	1.90	1.90	-0.09
$F_{802}^{(CO)}$	TPD	0.36	0.36	-0.24
GTSP				
F_{12}	TPD	909	909	0.01
$F_{39}^{(P_2O_5)}$	TPD	728	728	0.00

Table 4-131 Continued

Names	Unit	Industry Data	Results from the System	Percent Difference
GTSP				
F_{51}	TPD	2,259	2,259	0.00
F_{63}	TPD	29	29	-0.04
MAP and DAP				
$F_{40}^{(P_2O_5)}$	TPD	3,066	3,066	0.00
F_{42}	TPD	1,357	1,359	0.16
F_{52}	TPD	885	884	-0.05
F_{57}	TPD	5,666	5,666	0.00
Ammonium nitrate				
$F_{45}^{(HNO_3)}$	TPD	539	539	0.00
F_{44}	TPD	146	146	-0.21
$F_{56} + F_{62}^{(AN)}$	TPD	684	684	0.01
F_{56}	TPD	659	659	0.05
$F_{62}^{(AN)}$	TPD	25	25	0.86
UAN				
F_{54}	TPY	36,620	35,966	-1.78
F_{62}	TPY	30,072	30,702	2.10
Sales				
$F_{41}^{(P_2O_5)}$	TPD	38	38	0.00
F_{43}	TPD	164	162	-1.50

In summary, the complex model for the agricultural chemical complex accurately predicts the operating conditions, which agree with the industry data with an overall average difference of 0.25% from the industry data. These results illustrated the capability of the System to simulate a chemical production complex.

F. Summary

This chapter describes the detail process model for the chemical production complex in the lower Mississippi River corridor. The simulation of chemical production complex of existing plants in the Chemical Complex Analysis System has been validated using results from the industrial advisory group. The next chapter gives the detail results using the System for the chemical complex optimization.

CHAPTER V OPTIMAL IMPLEMENTATION OF CHEMICAL COMPLEX OPTIMIZATION

A. Introduction

Based on the results of this research, the optimal way to conduct chemical complex optimization is proposed, and this is tested with the chemical production complex in the lower Mississippi River corridor. Moreover, a Chemical Complex Analysis System is developed to facilitate engineer's effort in applying chemical complex optimization. This program incorporates the results of this research. In this chapter, the results from this research are described in detail.

B. Results of Application of Chemical Complex Analysis System

B-1. Chemical Production Complex Optimization

The Chemical Complex Analysis system has been applied to a chemical production complex in the lower Mississippi River Corridor. The diagram of plants in the agricultural chemical complex is shown in Figure 4.42, which was used to validate the System. The agricultural chemical complex has been extended to the chemical production complex using the existing plants in the lower Mississippi River corridor, which is called the base case of existing plants (Figure 3.3). There are thirteen production units plus associated utilities for power, steam and cooling water and facilities for waste treatment. Here, ammonia plants produce 0.75 million metric tons/year of carbon dioxide, and methanol, urea, and acetic acid plants consume 0.14 million metric tons/year of carbon dioxide. This leaves a surplus of 0.61 million metric tons/year of high quality carbon dioxide, as shown in Figure 3.3. This high purity carbon dioxide is being vented to the atmosphere now. A table showing the flow rates of all streams among the plants in the base case is given in Appendix D.

The characteristics of the base case are shown in Table 5-1. There are 270 equality constraints that describe material and energy balances for the plants. Also, there are 28 inequality constraints that describe the product demand, raw material availability, and capacities of the plants in the chemical complex.

Table 5-1 Base Case Characteristics

- 270 equality constraints that describe material and energy balances for the plants
- 28 inequality constraints that describe the product demand, availability of raw materials, and capacities of the plants in the chemical complex
- 326 variables
- 56 degrees of freedom

The chemical production complex shown in Figure 3.3 was expanded into a superstructure (Figure 3.4) by adding new chemical processes. These plants consumed the excess carbon dioxide being vented currently and gave alternative ways to produce phosphoric acid, and recover sulfur and sulfur dioxide from gypsum waste.

Fourteen potentially new processes for consuming CO_2 from Table 5-2 were selected and integrated into the superstructure based on the evaluations of HYSYS simulations (Indala, 2004). These processes include four processes for methanol production, two processes for propylene, and one process each for ethanol, DME, formic acid, acetic acid, styrene, methylamines, graphite and H_2, and synthesis gas.

Four other new processes that do not use CO_2 as a raw material were incorporated in the superstructure. Two additional plants were added to produce phosphoric acid. One is the electric furnace process, which has high-energy cost but produce phosphoric acid. In the other process (Haifa process), calcium phosphate ore reacts with hydrochloric acid to produce phosphoric acid. Also, there are two plants that use gypsum wastes to recover sulfur and sulfur dioxide. One reduces gypsum waste to sulfur dioxide that is recycled to the sulfuric acid plant. The other reduces gypsum waste to sulfur and sulfur dioxide that are recycled to the sulfuric acid plant. Thus, a total of eighteen new processes were included in the superstructure.

Table 5-2 Potentially New Processes Integrated into the Chemical Complex, from Indala (2004)

Product	Synthesis Route	Value Added Profit (cents/kg)	Reference
Methanol	CO_2 hydrogenation	2.8	Nerlov and Chokendorff, 1999
Methanol	CO_2 hydrogenation	3.3	Ushikoshi, 2002
Methanol	CO_2 hydrogenation	7.6	Jun, et al., 1998
Methanol	CO_2 hydrogenation	5.9	Bonivardi, et al., 1998
Ethanol	CO_2 hydrogenation	33.1	Higuchi, et al., 1998
Dimethyl Ether	CO_2 hydrogenation	69.6	Jun, et al., 2002
Formic Acid	CO_2 hydrogenation	64.9	Dinjus, 1998
Acetic Acid	From CH_4 and CO_2	97.9	Taniguchi, et al., 1998
Styrene	Ethylbenzene dehydrogenation	10.9	Mimura, et al., 1998
Methylamines	From CO_2, H_2, and NH_3	124	Arakawa, 1998
Graphite	Reduction of CO_2	65.6	Nishiguchi, et al., 1998
Hydrogen /Synthesis Gas	Methane reforming	17.2	Shamsi, 2002
Propylene	Propane dehydrogenation	4.3	Takahara, et al., 1998
Propylene	Propane dehydrogenation with CO_2	2.5	C & EN, June 2003, p. 15

A convenient way to show the plants in base case and the plants added to form the superstructure is given in Table 3-1. This expanded complex gives alternative ways to produce intermediates that reduce wastes and energy and consume greenhouse gases.

In summary, the superstructure includes three options for producing phosphoric acid, five options for producing methanol, two options each for producing acetic acid, styrene and propylene. It also includes two options for recovering sulfur and sulfur dioxide. It includes plants producing sulfuric acid, nitric acid, urea, urea ammonium nitrate solution (UAN), granular triple super phosphate (GTSP), mono- and di- ammonium phosphates (MAP and DAP), ethylbenzene, graphite, synthesis gas, DME, formic acid, ethanol, and methylamines [monomethyamine (MMA) and dimethylamine (DMA)].

To determine the optimum configuration of plants in the chemical complex, a value-added economic model given by the profit in Equation 5-1 was expanded to account for environmental and sustainable costs. Environmental costs are costs required to comply with federal and state environmental regulations including permits, monitoring emissions, fines, etc., as described in the AIChE/TCA report (Constable, et al., 2000). Sustainable costs are costs to society from damage to the environment by emissions discharged within permitted regulations. This extended value-added economic model is referred to as the “triple bottom line” and is the difference between sales and sustainable credits and economic costs (raw materials and utilities), environmental costs and sustainable costs as given by Equation 5-2. The sales prices for products and the costs of raw materials are given in Table 5-3 along with sustainable costs and credits. Also, the standard deviation of the prices and costs are given in Table 5-3 which are used in the sensitivity analysis.

$$\text{Profit} = \Sigma \text{ Product Sales} - \Sigma \text{ Raw Material Costs} - \Sigma \text{ Energy Costs} \qquad (5\text{-}1)$$

$$\text{Triple Bottom Line} = \Sigma\ \text{Product Sales} - \Sigma\ \text{Raw Material Costs} - \Sigma\ \text{Energy Costs} \quad (5\text{-}2)$$
$$- \Sigma\ \text{Environmental Costs} + \Sigma\ \text{Sustainable (Credits} - \text{Costs)}$$

$$\text{Triple Bottom Line} = \text{Profit} - \Sigma\ \text{Environmental Costs} + \Sigma\ \text{Sustainable (Credits} - \text{Costs)}$$

Environmental costs were estimated to be 67% of the raw material costs based on the data provided by Amoco, Dupont and Novartis in the AIChE/TCA report (Constable, et al., 2000). This report lists environmental costs and raw material costs as approximately 20% and 30% of the total manufacturing costs respectively.

Sustainable costs were estimated from results given for power generation in the AIChE/TCA report where CO_2 emissions had a sustainable cost of \$3.25 per metric ton of CO_2. As shown in Table 5-3, a cost of \$3.25 was charged as a cost to plants that emitted CO_2, and a credit of twice this cost (\$6.50) was given to plants that utilized CO_2. In this report SO_2 and NO_X emissions had sustainable costs of \$192 per metric ton of SO_2 and \$1,030 per metric ton of NO_X. In addition, for gypsum production and use, an arbitrary but conservative sustainable cost of \$2.5 per metric ton for gypsum production was used, and a credit of \$5.0 per metric ton for gypsum consumption was used.

For mixed integer optimization, relations among the binary variables and the logical constraints used in the System are given in Table 4-111. The upper bounds and lower bounds of the production capacities of all the plants in the chemical complex are shown in Table 4-112.

Table 5-3 Raw Material Costs, Product Prices and Sustainable Costs and Credits, Source: Constable, et al. (2000), Chemical Market Reporter, Camford Chemical Prices, Internet and C&EN (2003)

Raw Materials	Cost ($/mt)	Standard deviation ($/mt)	Sustainable Cost and Credits	Cost /Credit ($/mt)	Products	Price ($/mt)	Standard deviation ($/mt)
Natural gas	235	69.4	Credit for CO_2 consumption	6.50	Ammonia	224	17.7
Phosphate rock			Debit for CO_2 production	3.25	Methanol	271	43.2
Wet process	27	-	Debit for NO_x production	1,030	Acetic acid	1,030	36.6
Electric furnace	34	-	Debit for SO_2 production	192	GTSP	132	-
Haifa process	34	-	Credit for gypsum consumption	5.0	MAP	166	4.20
GTSP process	32	-	Debit for gypsum production	2.5	DAP	179	7.89
HCl	95	11.1			NH_4NO_3	146	6.66
Sulfur					Urea	179	17.4
Frasch	53	9.50			UAN	120	-
Claus	21	3.55			Phosphoric acid	496	-
Coke electric furnace	124	-			Hydrogen	1,030	252
Propane	180	-			Ethylbenzene	556	75.9
Benzene	303	60.3			Styrene	824	94.7
Ethylene	565	95.4			Propylene	519	66.0
Reducing gas	75	-			Formic acid	690	-
Wood gas	88	-			MMA	1,610	-
					DMA	1,610	-
					DME	946	-
					Ethanol	933	23.1
					Toluene	384	47.7
					Graphite	904	82.0
					Fuel gas	784	-
					CO	45	13.3

The characteristics of the superstructure are shown in Table 5-4. The superstructure has 735 continuous variables, 23 integer variables, and 601 equality constraints that describe material and energy balances for the plants. Also, there are 77 inequality constraints that describe availability of raw materials, demand for products, capacities of the plants, and logical relations in the chemical complex. The degrees of freedom are 134, and the optimal solution obtained with the Chemical Complex Analysis System is discussed below.

Table 5-4 Superstructure Characteristics

- 601 equality constraints that describe material and energy balances for the plants
- 77 inequality constraints that describe availability of raw materials, demand for product, capacities of the plants, and logical relations in the chemical complex
- 735 continuous variables
- 23 integer variables
- 134 degrees of freedom

The optimum configuration of plants was obtained from the superstructure by maximizing the triple bottom line, Equation 5-2, subject to the equality and inequality constraints using the Chemical Complex Analysis System. The optimal structure from the superstructure is shown in Figure 5.1, and a convenient way to show the new plants in the optimal structure is given in Table 5-5. Seven new processes in the optimal structure were selected from eighteen new processes in the superstructure. These included acetic acid, graphite, formic acid, methylamines, propylene (2) and synthesis gas production. The new acetic acid process replaced the commercial acetic acid plant in the chemical complex. The processes for dimethyl ether, styrene, and methanol were not selected in the optimal structure. It was more profitable to have the

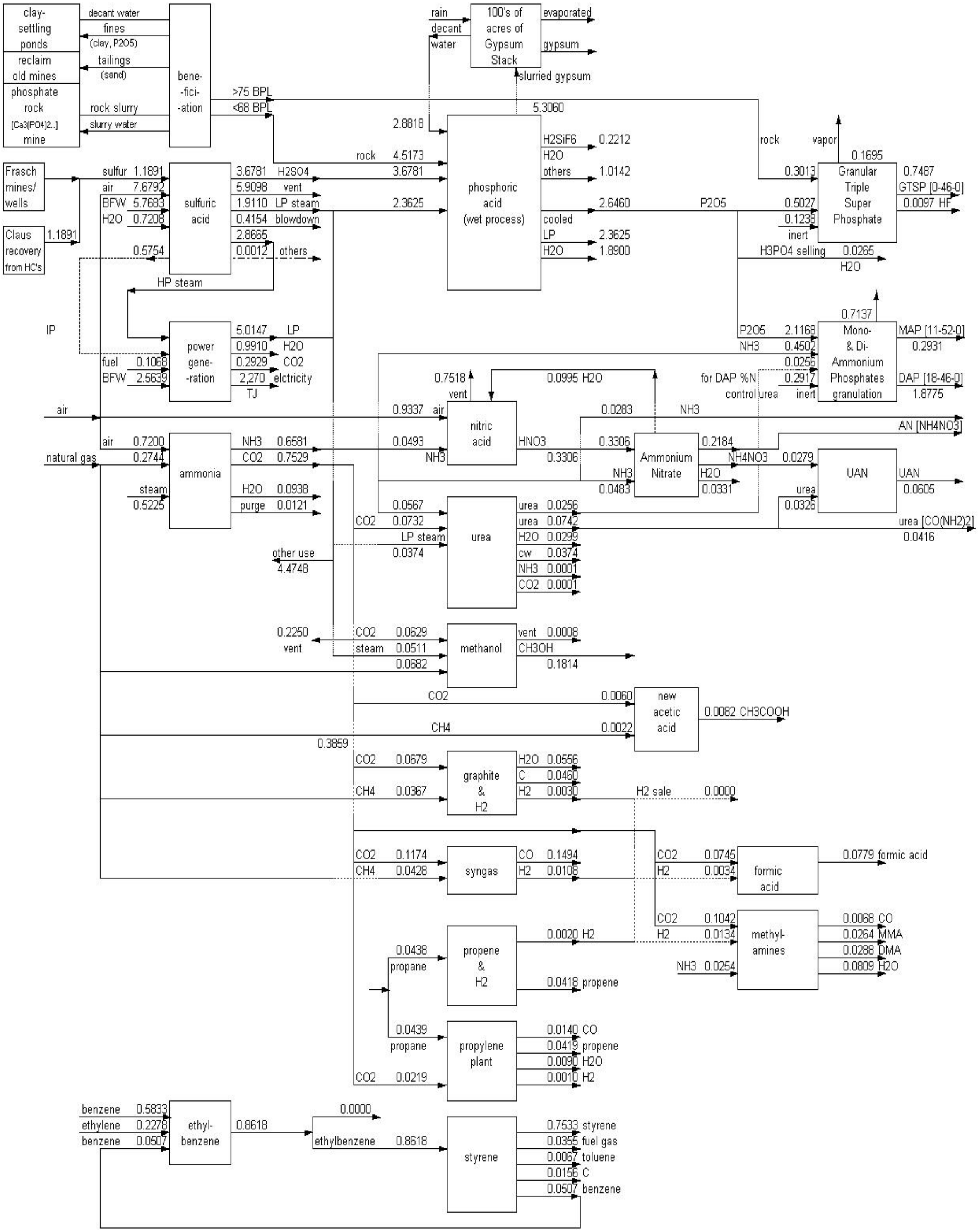


Figure 5.1 Optimal Configuration of the Chemical Production Complex, Flow Rates Million Metric Tons Per Year

corresponding commercial processes present. The commercial process for methanol does not use expensive hydrogen as a raw material, but the new methanol processes does. A table showing the flow rates of all streams among the plants in the optimal structure is given in Appendix D.

Table 5-5 Plants in the Optimal Structure from the Superstructure

Existing Plants in the Optimal Structure	New Plants in the Optimal Structure
Ammonia	Formic acid
Nitric acid	Acetic acid – new process
Ammonium nitrate	Methylamines (MMA and DMA)
Urea	Graphite
UAN	Hydrogen/synthesis gas
Methanol	Propylene from CO_2
Granular triple super phosphate (GTSP)	Propylene from propane dehydrogenation
MAP and DAP	
Contact process for Sulfuric acid	New Plants Not in the Optimal Structure
Wet process for phosphoric acid	Methanol – Bonivardi, et al., 1998
Ethylbenzene	Methanol – Jun, et al., 1998
Styrene	Methanol – Ushikoshi, et al., 1998
Power generation	Methanol – Nerlov and Chorkendorff, 1999
	Ethanol
Existing Plants Not in the Optimal Structure	Dimethyl ether
	Styrene - new method
Acetic acid	Electric furnace process for phosphoric acid
	Haifa process for phosphoric acid
	SO_2 recovery from gypsum waste
	S and SO_2 recovery from gypsum waste

Comparison of the sales and costs associated with the triple bottom line, Equation 5-2, are shown in Table 5-6 for the base case and the optimal structure. The triple bottom line increased from $343 to $506 million per year or about 48% from the base case to the optimal structure. Sales increased from additional products from carbon dioxide, and there were corresponding increases in the other costs associated with producing these products by the companies. Cost to society improved since sustainable costs decreased from \$18 to \$15 million per year from the credits given for using carbon dioxide and increased energy efficiency.

The increased use of carbon dioxide is shown in Table 5-7 for the optimal structure. However, it was not optimal to consume all of the carbon dioxide available, and 0.22 million metric tons per year is vented to the atmosphere, down by 0.39 million metric tons per year or 64%.

Table 5-6 Sales and Costs Associated with the Triple Bottom Line for the Base Case and Optimal Structure

	Base Case million dollars/year	Optimal Structure million dollars/year
Income from Sales	1,277	1,508
Economic Costs (Raw Materials and Utilities)	554	602
Raw Material Costs	542	577
Utility Costs	12	25
Environmental Cost (67% of Raw Material Cost)	362	385
Sustainable Credits (+)/Costs (-)	-18	-15
Triple Bottom Line	343	506

Table 5-7 Carbon Dioxide Consumption in Bases Case and Optimal Structure

	Base Case million metric tons/year	Optimal Structure million metric tons/year
CO_2 produced by NH_3 plant	0.75	0.75
CO_2 consumed by methanol, urea and other plants	0.14	0.53
CO_2 vented to atmosphere	0.61	0.22

Six of the seven new processes present in the optimal structure use CO_2 as a raw material as shown in Tables 5-5 and 5-8. In Table 5-8, the optimal capacities are given for the plants in the optimum structure of the chemical production complex. Also shown in this table is the energy used or produced for each process and the total

Table 5-8 Comparison of Capacities for the Base Case and Optimal Structure

Plant name	Capacity (upper-lower bounds) (mt/year)	Base case Capacity (mt/year)	Energy Requirement (TJ/year)	Optimal Capacity (mt/year)	Energy Requirement (TJ/year)
Ammonia	329,000-658,000	658,000	3,820	658,000	3,820
Nitric acid	89,000-178,000	178,000	-775	178,000	-775
Ammonium nitrate	113,000-227,000	227,000	229	227,000	229
Urea	49,900-99,800	99,800	128	99,800	128
Methanol	91,000-181,000	181,000	2,165	181,000	2,165
UAN	30,000-60,000	60,000	0	60,000	0
MAP	146,000-293,000	293,000		293,000	
DAP	939,000-1,880,000	1,880,000	1,901	1,880,000	1,901
GTSP	374,000-749,000	749,000	1,312	749,000	1,312
Sulfuric acid	1,810,000-3,620,000	3,620,000	-14,642	3,620,000	-14,642
Wet process phosphoric acid	635,000-1,270,000	1,270,000	5,181	1,270,000	5,181
Ethylbenzene	431,000-862,000	862,000	-755	862,000	-755
Styrene	386,000-771,000	753,000	3,318	753,000	3,318
Acetic acid	4,080-8,160	8,160	268	0	0
Electric furnace phosphoric acid	635,000-1,270,000	na	na	0	0
Haifa phosphoric acid	635,000-1,270,000	na	na	0	0
New Acetic acid	4,090-8,180	na	na	8,180	8
SO_2 recovery from gypsum	987,000-1,970,000	na	na	0	0
S and SO_2 recovery from gypsum	494,000-988,000	na	na	0	0
Graphite and H_2 from CO_2 and CH_4	230,000-460,000	na	na	46,000	1,046
Syngas	6,700-13,400	na	na	10,800	691
Propene and H_2	20,900-41,800	na	na	41,800	658
Propene using CO_2	21,000-41,900	na	na	41,900	413
New Styrene	181,000-362,000	na	na	0	0
New methanol – Bonivardi	240,000-480,000	na	na	0	0
New methanol – Jun	240,000-480,000	na	na	0	0

Table 5-8 Continued

Plant name	Capacity (upper-lower bounds) (mt/year)	Base case Capacity (mt/year)	Energy Requirement (TJ/year)	Optimal Capacity (mt/year)	Energy Requirement (TJ/year)
New methanol – Nerlov	240,000-480,000	na	na	0	0
New methanol – Ushikoshi	240,000-480,000	na	na	0	0
Formic acid	39,000-78,000	na	na	78,000	14
Methylaimines	13,200-26,400	na	na	26,400	1,079
Ethanol	52,000-104,000	na	na	0	0
Dimethyl ether	22,900-45,800	na	na	0	0
Ammonia sale		53,600		28,300	
Ammonium Nitrate sale		218,000		218,000	
Urea sale		41,600		41,600	
Wet process phosphoric acid sale		12,700		12,700	
Ethylbenzene sale		0		0	
CO_2 vented		612,000		225,000	
Total energy requirement			2,150		5,791

energy required for the complex. With the additional plants in the optimal structure the energy required increased from 2,150 to 5,791 TJ/year. This is reflected in the increased utility cost shown in Table 5-6 going from \$12 to \$25 million per year. This additional energy is supplied from firing boilers with natural gas that has a sustainable cost of \$3.25 per metric ton. As shown in Table 5-8 the sulfuric acid plant is an important source of energy as steam, and operating this plant for steam production is as important as production of sulfuric acid.

Two extensions to the optimal complex were evaluated. In one, the optimum was determined requiring that all of the CO_2 from the ammonia plant be consumed. In the other, the optimum was determined requiring that all of the CO_2 from the ammonia plant be consumed and the ammonia plant be operated at full capacity. These results are summarized in Table 5-9 along with the results in Table 5-6. The triple bottom line decreased to \$467 million per year having all of the CO_2 from the ammonia plant be consumed, and it decreased further to \$412 million per year with the additional requirement that the ammonia plant be operated at full capacity. These declines are a result of changes in sales and all of the associated costs as shown in Table 5-9.

A third extension had the sustainable credits be equal to the sustainable costs, \$3.25 per metric ton of carbon dioxide rather than double, \$6.50 per metric ton. These results are shown in Table 5-9, and the sustainable costs increased from \$15 to \$17 million per year as would be expected.

These case study results point out the need for methods that can give general evaluations. Results are needed to determine maximizing companies' profits and minimizing costs to society, and multicriteria optimization can provide this information. In addition, solutions are needed that incorporate the sensitivity of the optimal structure to prices and economic, environmental and sustainable costs; and Monte Carlo simulation is the appropriate procedure to generate these results. These methods have been applied, and the results are described in the next sections.

B-2. Multiobjective Optimization of Chemical Production Complex

The objective is to find optimal solutions that maximize companies' profits and minimize costs to society. Companies' profits are sales minus economic and environmental costs. Economic costs include raw material, utilities, labor, and other

Table 5-9 Results for Base Case, Optimal Structure and Extensions

	Base Case million dollars /year	Optimal million dollars /year	Use all CO_2 million dollars /year	Max NH_3 Plant million dollars /year	Equal CO_2 Credit and Cost million dollars/year
Income from Sales	1,277	1,508	1,392	1,174	1,508
Economic Costs (Raw Materials and Utilities)	554	602	560	460	602
Raw Material Costs	542	577	533	435	577
Utility Cost	12	25	27	25	25
Environmental Cost (67% of Raw Material Cost)	362	385	355	290	385
Sustainable Credits (+) /Costs(-)	-18	-15	-10	-12	-17
Triple Bottom Line	343	506	467	412	504
	Million mtons/year	Million mtons/year	Million mtons/year	million mtons/year	million mtons/year
CO_2 produced by NH_3 Plant	0.75	0.75	0.56	0.75	0.75
CO_2 consumed by methanol, urea and other plants	0.14	0.53	0.56	0.75	0.53
CO_2 vented to atmosphere	0.61	0.22	0.0	0.0	0.22

manufacturing costs. Environmental costs include permits, monitoring of emissions, fines, etc. The costs to society are measured by sustainable costs. These costs are from damage to the environment by emissions discharged within permitted regulations.

Sustainable credits are awarded for reductions in emissions as shown in Table 5-3, and are similar to emissions trading credits.

The multicriteria optimization problem can be stated as in terms of profit, P, and sustainable credits/costs, S, for theses two objectives in Equation 5-3.

Max: $P = \Sigma$ Product Sales - Σ Economic Costs - Σ Environmental Costs (5-3)
$S = \Sigma$ Sustainable (Credits – Costs)

Subject to: Multi-plant material and energy balances
Product demand, raw material availability, plant capacities

Multicriteria optimization obtains solutions that are called efficient or Pareto optimal solutions. These are optimal points where attempting to improving the value of one objective would cause another objective to decrease. To locate Pareto optimal solutions, multicriteria optimization problems are converted to one with a single criterion by parametric approach method, which is by applying weights to each objective and optimizing the sum of the weighted objectives. The multicriteria mixed integer optimization problem becomes:

Max: $w_1P + w_2S$ (5-4)

Subject to: Multi-plant material and energy balances
Product demand, raw material availability, plant capacities

The Chemical Complex Analysis System was used to determine the Pareto optimal solutions for the weights using $w_1 + w_2 = 1$ given by Equation 5-4, and these results are shown in Figure 5.2. Company profits are an order of magnitude larger than sustainable credits/costs. Sustainable credits/costs decline and company profits increase as the weight, w_1, on company profits increase. For example, when $w_1 = 1$, this is the optimal solution shown in Table 5-10 for P = \$520.6 and S = \$-14.76

million per year. The optimal solution with $w_1 = 0$ gave P = \$94.37 and S = \$23.24 million per year.

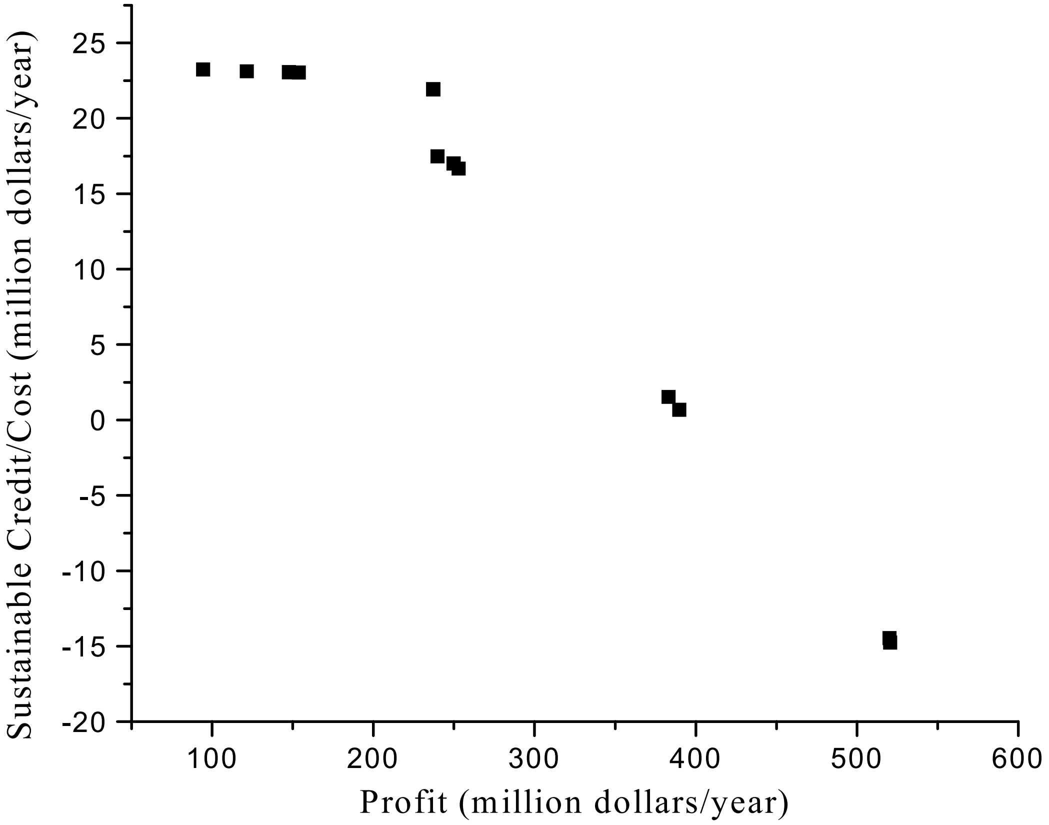


Figure 5.2 Optimal Solutions Generated by Multicriteria Optimization

The points shown in Figure 5.2 are the Pareto optimal solutions for w_1 from 0 to 1.0 for increments of 0.001. The values for w_1 equal to 0 and 1.0 and some intermediate ones are shown in Table 5-10. It shows that the sustainable costs become credits of \$0.68 million per year for a profit of \$389.8 million per year.

Table 5-10 Several Values of the Pareto Optimal Solutions shown in Figure 5.2

Profit (million dollars/year)	Sustainable Credits/Costs (million dollars/year)	Weight (w_1)
520.6	-14.76	1
520.1	-14.45	0.417
389.8	0.68	0.172
383.1	1.53	0.115
252.9	16.68	0.104
249.8	17.02	0.103
239.7	17.48	0.039
237.1	21.93	0.037
153.7	23.04	0.013
147.6	23.07	0.004
121.5	23.12	0.002
94.37	23.24	0

The chemical production complex configurations of the Pareto optimal solutions for w_1 from 0 to 1.0 for increment of 0.001 are shown in Table 5-11. If a process is selected, the binary variable associated with the process is 1, otherwise 0. For each processes in Table 5-11, the sums of the binary variable values for the corresponding w_1 range are shown, along with the total summation of the times the process was selected. New acetic acid process always replaced the conventional one. The conventional methanol always operated instead of the four potentially new methanol processes. Synthesis gas, formic acid, propylene from CO_2, propylene from propane dehydrogenation, graphite, wet process phosphoric acid, and ethyl benzene process always operated. Ethanol, electric furnace phosphoric acid, and Haifa process phosphoric acid never operated. Only when w_1 was very small (0-0.150), SO_2 recovery from gypsum, S and SO_2 recovery from gypsum, new styrene, and dimethyl ether started operation. Methylamines and styrene processes always ran except that when w_1 was very small (0-0.150). Hence, the optimal structure is affected, but it did not change significantly (Table 5-11). It is another decision to determine the specific value of the weight that is acceptable to all concerned.

Table 5-11 Optimal Structure Changes in Multicriteria Optimization (Number of Times out of 1,001 a Process is Selected)

Processes	w_1							
	0.000-0.149	0.150-0.299	0.300-0.449	0.450-0.599	0.600-0.749	0.750-0.899	0.900-1.000	Sum
Electric furnace phosphoric acid (Y_1)	0	0	0	0	0	0	0	0
Acetic acid (Y_{11})	0	0	0	0	0	0	0	0
New acetic acid (Y_{12})	150	150	150	150	150	150	101	1,001
SO_2 recovery from gypsum (Y_{13})	112	23	0	0	0	0	0	135
S and SO_2 recovery from gypsum (Y_{14})	38	0	0	0	0	0	0	38
Methanol (Y_{16})	150	150	150	150	150	150	101	1,001
Haifa process phosphoric acid (Y_2)	0	0	0	0	0	0	0	0
Propylene from CO_2 (Y_{23})	150	150	150	150	150	150	101	1,001
Propylene from propane dehydrogenation (Y_{24})	150	150	150	150	150	150	101	1,001
Synthesis gas (Y_{27})	150	150	150	150	150	150	101	1,001
Formic acid (Y_{29})	150	150	150	150	150	150	101	1,001
Wet process phosphoric acid (Y_3)	150	150	150	150	150	150	101	1,001
Methylamines (Y_{30})	149	150	150	150	150	150	101	1,000
Methanol (Jun, et al., 1998) (Y_{31})	0	0	0	0	0	0	0	0
Methanol (Bonivardi, et al., 1998) (Y_{32})	0	0	0	0	0	0	0	0
Methanol (Nerlov and Chorkendorff, 1999) (Y_{33})	0	0	0	0	0	0	0	0
Methanol (Ushikoshi, et al., 1998) (Y_{34})	0	0	0	0	0	0	0	0

Table 5-11 Continued

Processes	w_1							
	0.000-0.149	0.150-0.299	0.300-0.449	0.450-0.599	0.600-0.749	0.750-0.899	0.900-1.000	Sum
New styrene (Y_{35})	14	0	0	0	0	0	0	14
Ethanol (Y_{37})	0	0	0	0	0	0	0	0
Dimethyl ether (Y_{38})	40	0	0	0	0	0	0	40
Graphite (Y_{39})	150	150	150	150	150	150	101	1,001
Styrene (Y_{40})	136	150	150	150	150	150	101	987
Ethyl benzene (Y_{41})	150	150	150	150	150	150	101	1,001

In addition, the cases with different increments are obtained. The general results are the smaller the increment, the more Pareto points are. And profit and sustainable credit cannot be maximized at same time.

In summary, the multicriteria optimization demonstrated the relationship of different objectives, which can be used by the decision maker.

B-3. Monte Carlo Simulation of Chemical Production Complex

Monte Carlo simulation was used to determine the sensitivity of the optimal solution to the costs and prices used in the triple bottom line. One of the results is the cumulative probability distribution, a curve of the probability as a function of the triple bottom line. A value of the cumulative probability for a given value of the triple bottom line is the probability that the triple bottom line will be equal to or less than that value. This curve is used to determine upside and downside risks.

For a Monte Carlo simulation, mean prices and costs along with an estimate of their standard deviations are required. The costs and prices in Table 5-3 were used, and standard deviations estimated from cost and price fluctuations from the sources were given in Table 5-3 over a three- to five-year period. Sustainable costs and credits were constant, and sensitivity to these values is to be determined in a subsequent evaluation.

According to the uncertainty about the mean, the sample size of Monte Carlo simulation can be selected based on the method described in Chapter III. For the confidence α=95%, the deviation c for the unit normal enclosing probability 95% is 1.96. First, make Monte Carlo run 20 times, get an initial estimate s^2; then, use $m > \left(\frac{2cs}{w}\right)^2$ to estimate the number of samples needed in total to reduce the confidence interval to the presumed width w (Table 5-12)

Table 5-12 Sample Size Determined by the Uncertainty about the Mean

Triple Bottom Line (million dollars per year)	Triple Bottom Line (million dollars per year)	Triple Bottom Line (million dollars per year)
352.61	565.67	402.40
739.19	623.44	505.12
424.44	305.61	357.75
622.90	552.84	619.30
545.34	609.51	458.49
392.36	582.20	901.19
503.37	391.44	
s^2=21,074		
$w = 18$		
$m > \left(\frac{2cs}{w}\right)^2 = \left(\frac{2\times1.96\times\sqrt{21{,}074}}{18}\right)^2 = 999.5 \approx 1{,}000$		

Another way to determine the sample size is from estimating confidence interval for fractiles. Here, confidence α=95% is still used, then the deviation c for the unit normal enclosing probability 95% is 1.96. According to the method described in Chapter III, p=50% fractile is considered with Δp=3.1%. Based on Equation 3-13, the sample size is $m = p(1-p)(\frac{c}{\Delta p})^2 = 0.5 \times (1-0.5)(\frac{1.96}{0.031})^2 = 999.4 \approx 1{,}000$, i.e., 95% confidence of $Y_{0.485}<Y_{0.50}<Y_{0.515}$, where $Y_{0.485}$ and $Y_{0.515}$ are sample values in 1,000 Monte Carlo runs.

Hence, Monte Carlo simulations were run for a total of 1,000 iterations, and the cumulative probability distribution shown in Figure 5.3 was obtained. The mean for the triple bottom line was $513 million/year, and the standard deviation was $109 million/year. For the 1,000 samples, the maximum was $901 million/year, and the minimum was $232 million/year. The triple bottom line from Table 5-6 is $506 million per year which is statistically the same as the mean from the Monte Carlo simulation, $513 million per year.

Referring to Figure 5.3, a value of the cumulative probability for a given value of the triple bottom line is the probability that the triple bottom line will be equal to or less that value. For example, interpolated from Figure 5.3, there is 50% probability that the profit is equal to or less than $510 million per year. This is statistically the same value that was obtained for the optimal structure in Table 5-6 of $506 million per year as is required for a Gaussian probability distribution.

Now a range of values is available for the optimum triple bottom line that can be used to assess the risk of proceeding as measured by the cumulative probability distribution. For example, there is 95% confidence that the mean $513 million/year falls in the range of $513-18/2=504 to $513+18/2=522 million/year. Also, from Figure 5.5, with 95% confidence, $Y_{0.485}$ ($505 million/year) < $Y_{0.50}$ ($510 million/year) < $Y_{0.515}$ ($515 million/year).

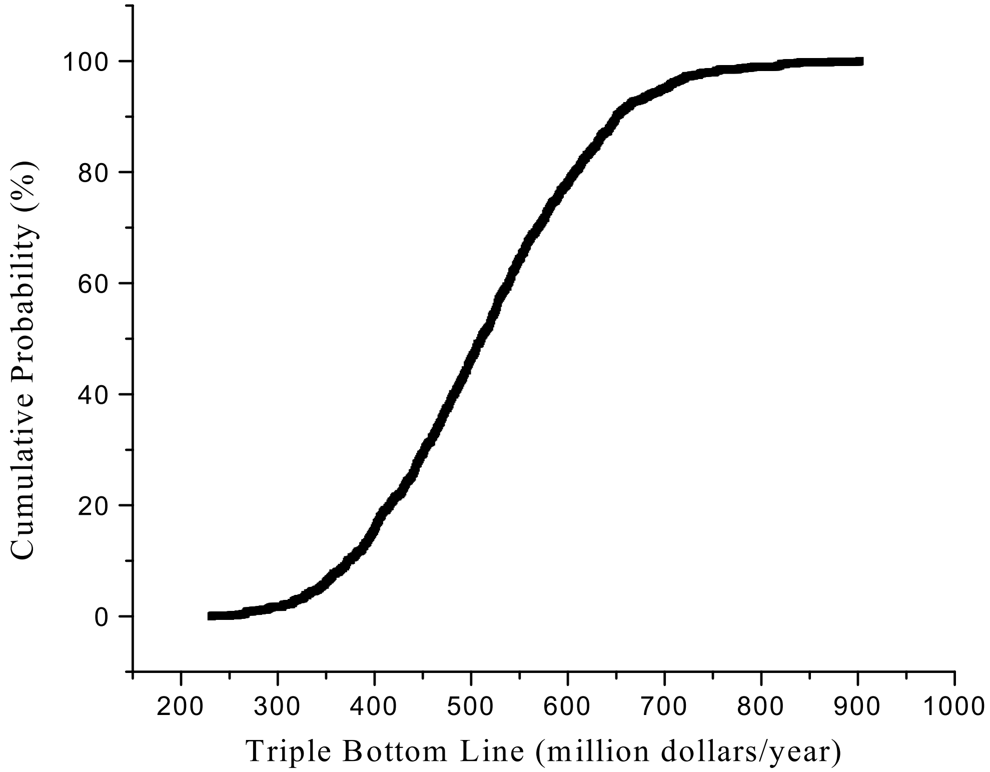


Figure 5.3 Cumulative Probability Distribution for the Triple Bottom Line of the Optimal Structure

The chemical production complex configurations of Monte Carlo simulation solutions for 1,000 samples are shown in Table 5-13. If a process is selected, the binary variable associated with the process is 1, otherwise 0. For each processes in Table 5-13, the sums of the binary variable values for the corresponding iteration range are shown, along with the total summation of the times the process was selected. New acetic acid process always replaced the conventional one. The conventional methanol almost always operated instead of the four potentially new methanol processes. The conventional styrene almost always operated instead of the potentially new styrene process. Synthesis gas, formic acid, propylene from CO_2, graphite, wet

Table 5-13 Optimal Structure Changes in Monte Carlo Simulation (Number of Times out of 1,000 a Process is Selected)

Processes	Monte Carlo Simulation (Iterations)							
	1-150	151-300	301-450	451-600	601-750	751-900	901-1000	Sum
Electric furnace phosphoric acid (Y_1)	0	0	0	0	0	0	0	0
Acetic acid (Y_{11})	0	0	0	0	0	0	0	0
New acetic acid (Y_{12})	150	150	150	150	150	150	100	1,000
SO_2 recovery from gypsum (Y_{13})	0	0	0	0	0	0	0	0
S and SO_2 recovery from gypsum (Y_{14})	0	0	0	0	0	0	0	0
Methanol (Y_{16})	138	133	131	129	125	132	85	873
Haifa process phosphoric acid (Y_2)	0	0	0	0	0	0	0	0
Propylene from CO_2 (Y_{23})	150	150	150	150	150	150	100	1,000
Propylene from propane dehydrogenation (Y_{24})	149	150	150	150	150	150	99	998
Synthesis gas (Y_{27})	150	150	150	150	150	150	100	1,000
Formic acid (Y_{29})	150	150	150	150	150	150	100	1,000
Wet process phosphoric acid (Y_3)	150	150	150	150	150	150	100	1,000
Methylamines (Y_{30})	150	150	150	150	150	150	100	1,000
Methanol (Jun, et al., 1998) (Y_{31})	0	0	0	0	0	0	0	0
Methanol (Bonivardi, et al., 1998) (Y_{32})	0	0	0	0	0	0	0	0
Methanol (Nerlov and Chorkendorff, 1999) (Y_{33})	0	0	0	0	0	0	0	0
Methanol (Ushikoshi, et al., 1998) (Y_{34})	0	0	0	0	0	0	0	0
New styrene (Y_{35})	0	1	1	0	0	0	0	2
Ethanol (Y_{37})	0	0	0	0	0	0	0	0
Dimethyl ether (Y_{38})	0	0	0	0	0	0	0	0
Graphite (Y_{39})	150	150	150	150	150	150	100	1,000
Styrene (Y_{40})	134	138	138	145	141	140	87	923
Ethyl benzene (Y_{41})	136	142	142	146	142	142	88	938

process phosphoric acid, and methylamines process always operated. Ethanol, electric furnace phosphoric acid, Haifa process phosphoric acid, SO_2 recovery from gypsum, S and SO_2 recovery from gypsum, dimethyl ether, and four new methanol processes never operated. New styrene process only started operation twice out of one thousand iterations. Ethyl benzene, and propylene from propane dehydrogenation almost always ran. Hence, the optimal structure is affected, but it did not change significantly (Table 5-13).

B-4. Pollution Index of Chemical Production Complex

The Pollution Index program can be applied to the complex and identify plants that should be eliminated or modified to reduce emissions. This part of work is to be finished in the near future.

C. Previous Results of Chemical Complex Optimization of Chemical Production Complex in Reverse Chronological Order

C-1. Extension of Chemical Production Complex with CO_2 Consuming Processes

Two additional evaluations have been performed using the System. One uses one potentially new methanol plant instead of four plants. The other does not include the CO_2 consuming process except for acetic acid. The brief description for each case is given in the next sections.

C-1-1. Extension 1

The base case was same as the current one (Figure 3.3). For superstructure (Figure 5.4), the difference compared to the current one (Figure 3.4) is only one new methanol plant was included in the superstructure instead of four new methanol plants. A summary of plants in the base case and superstructure was given in Table 5-14.

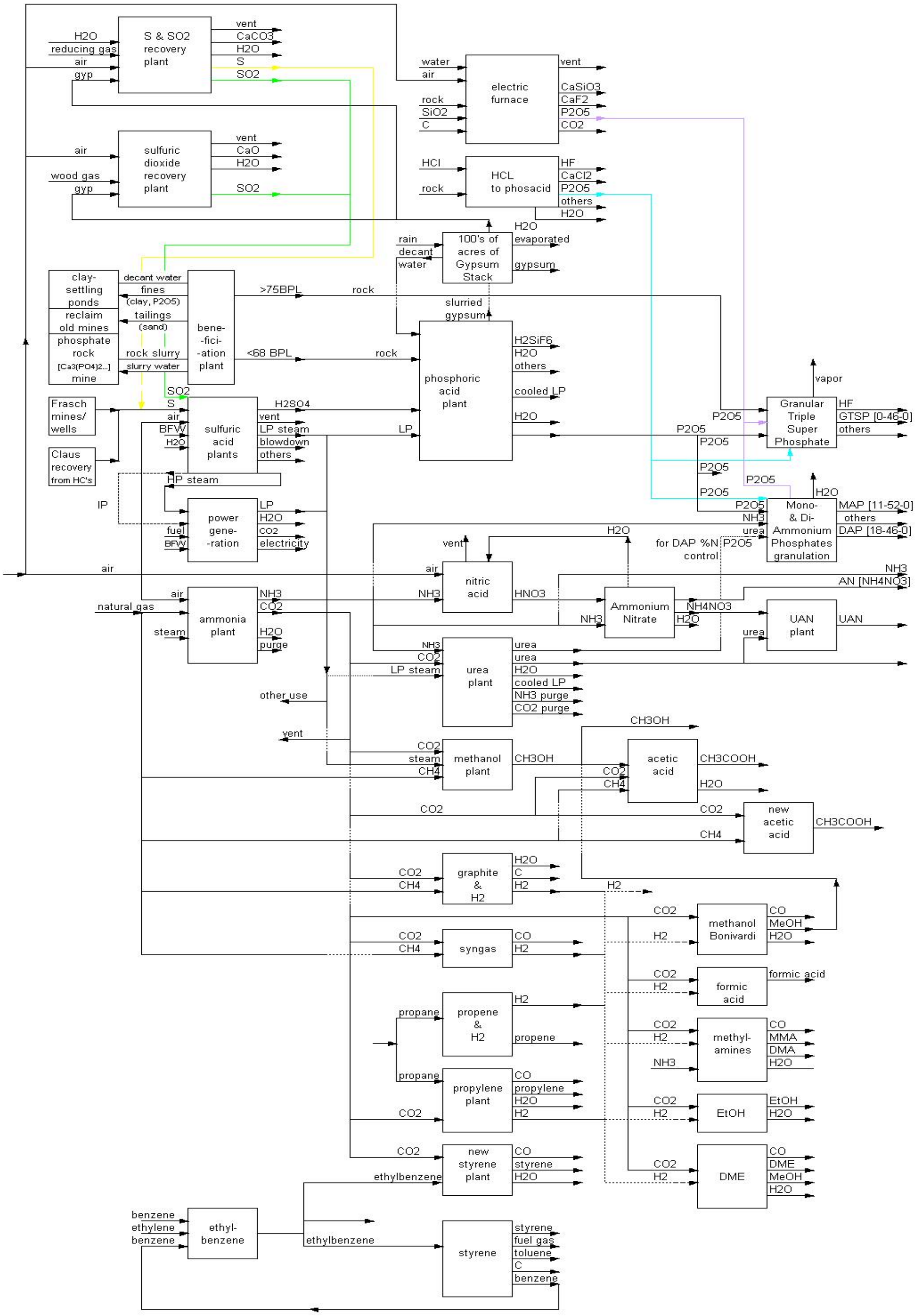


Figure 5.4 Chemical Production Complex in the Lower Mississippi River Corridor, Superstructure (Extension 1)

Table 5-14 Processes in Chemical Production Complex Base Case and Superstructure (Extension 1)

Plants in the Base Case	Plants Added to Form the Superstructure
Ammonia	Methanol – Bonivardi, et al., 1998
Nitric acid	Ethanol
Ammonium nitrate	Dimethyl ether
Urea	Formic acid
UAN	Acetic acid – new process
Methanol	Styrene – new process
Granular triple super phosphate (GTSP)	Methylamines (MMA and DMA)
MAP and DAP	Graphite and hydrogen
Contact process for Sulfuric acid	Hydrogen/synthesis gas
Wet process for phosphoric acid	Propylene from CO_2
Acetic acid - standard method	Propylene from propane dehydrogenation
Ethyl benzene	Electric furnace process for phosphoric acid
Styrene	Haifa process for phosphoric acid
Power generation	SO_2 recovery from gypsum waste
	S and SO_2 recovery from gypsum waste

For mixed integer optimization, relations among the binary variables and the logical constraints used in the System are given in Table 5-15. Compared to Table 4-111, the only difference was that there were no binary variables of Y_{31}, Y_{33} and Y_{34}, which were associated three other new methanol plants.

The characteristics of the superstructure were shown in Table 5-16. The superstructure has 690 continuous variables, 20 integer variables, and 564 equality constraints that describe material and energy balances for the plants. Also, there are 71 inequality constraints that describe availability of raw materials, demand for products, capacities of the plants, and logical relations in the chemical complex. The degrees of freedom are 126, and the optimal solution obtained with the Chemical Complex Analysis System is discussed below.

The optimum configuration of plants was obtained from the superstructure by maximizing the triple bottom line economic model subject to the equality and inequality constraints using the Chemical Complex Analysis System. The optimal structure from the superstructure is same as the one shown in Figure 5.1 and in Table 5-5. The discussion about the optimal solution is also same as the current results in the previous section, except that there were no three potentially new methanol plants from Jun, Nerlov and Ushikoshi, respectively.

Table 5-15 Logical Relations Used to Select the Optimal Structure (Extension 1)

Logic Expression	Logic Meaning
$Y_{11} + Y_{12} \leq 1$	At most one of these two acetic acid plants is selected.
$Y_{13} + Y_{14} \leq Y_3$	At most one of these two S and SO_2 recovery plants is selected only if phosphoric acid (wet process) is selected.
$Y_{16} + Y_{32} \leq 1$	At most one of these two methanol plants is selected.
$Y_{11} \leq Y_{16} + Y_{32}$	Only if at least one of these two methanol plants is selected, the conventional acetic acid may be selected.
$Y_{35} + Y_{40} \leq Y_{41}$	At most one of these two styrene plants is selected only if ethylbenzene plant is selected.
$Y_{29} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of these four plants with H_2 production is selected, the formic acid plant may be selected.
$Y_{30} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of these four plants with H_2 production is selected, the methylamines plant may be selected.
$Y_{32} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of these four plants with H_2 production is selected, the new methanol plant may be selected.
$Y_{37} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of these four plants with H_2 production is selected, the ethanol plant may be selected.
$Y_{38} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of these four plants with H_2 production is selected, the DME plant may be selected.

Table 5-16 Superstructure Characteristics (Extension 1)

- 564 equality constraints that describe material and energy balances for the plants
- 71 inequality constraints that describe availability of raw materials, demand for product, capacities of the plants, and logical relations in the chemical complex
- 690 continuous variables
- 20 integer variables
- 126 degrees of freedom

C-1-2. Extension 2

The base case was same as the current one (Figure 3.3). Compared with the current superstructure (Figure 3.4), the only difference with the superstructure of Extension 2 is no CO_2 consuming processes except for acetic acid (Figure 5.5). A summary of plants in the base case and superstructure was given in Table 5-17. Relations among the binary variables and the logical constraints used in the System are given in Table 5-18.

Table 5-17 Processes in Chemical Production Complex Base Case and Superstructure (Extension 2)

Plants in the Base Case	Plants Added to Form the Superstructure
Ammonia Nitric acid Ammonium nitrate Urea UAN Methanol Granular triple super phosphate (GTSP) MAP and DAP Contact process for Sulfuric acid Wet process for phosphoric acid Acetic acid - standard method Ethyl benzene Styrene Power generation	Acetic acid – new process Electric furnace process for phosphoric acid Haifa process for phosphoric acid SO_2 recovery from gypsum waste S and SO_2 recovery from gypsum waste

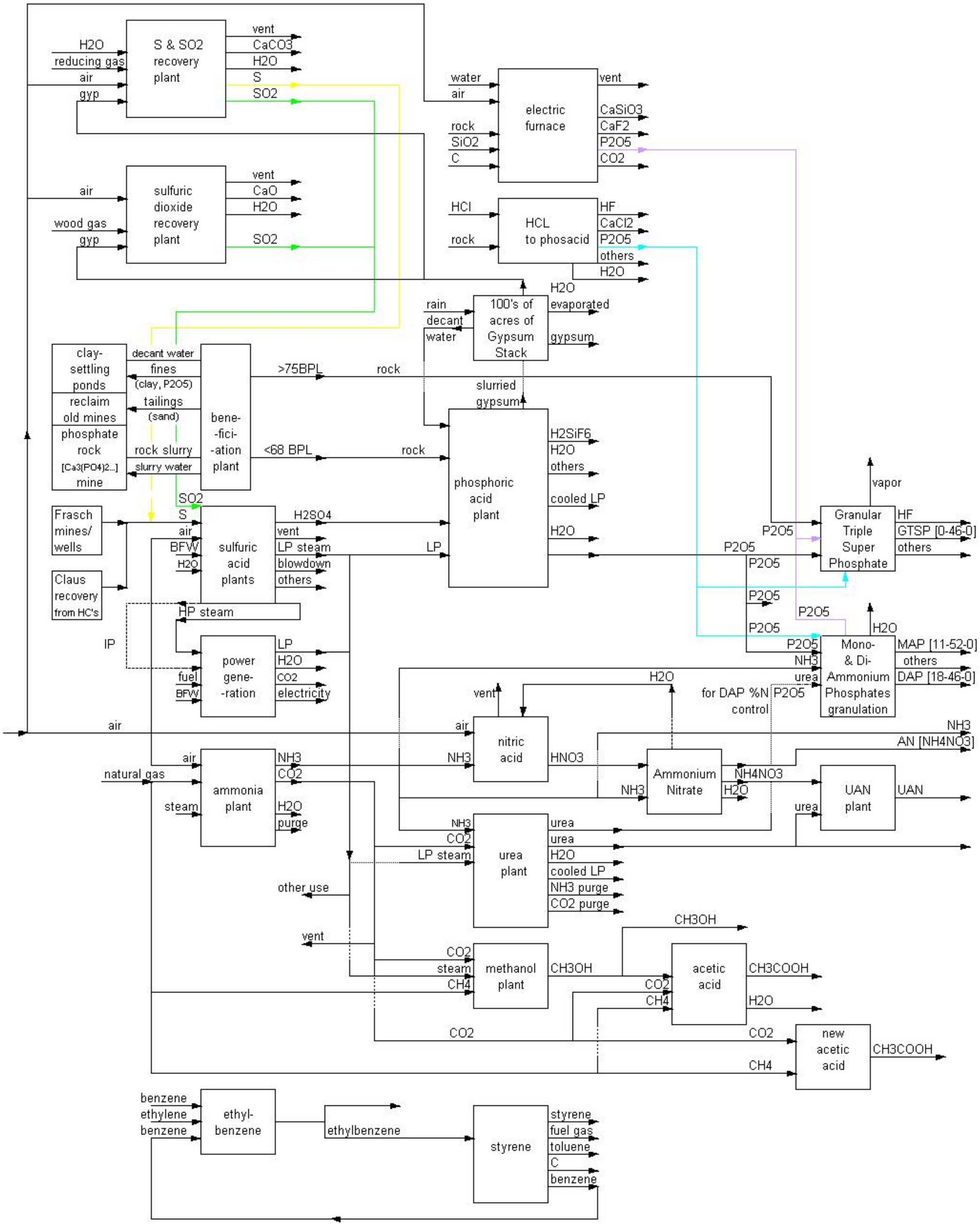


Figure 5.5 Chemical Production Complex in the Lower Mississippi River Corridor, Superstructure (Extension 2)

Table 5-18 Logical Relations Used to Select the Optimal Structure (Extension 2)

Logic Expression	Logic Meaning
$Y_{11} + Y_{12} \leq 1$	At most one of these two acetic acid plants is selected.
$Y_{13} + Y_{14} \leq Y_3$	At most one of these two S and SO_2 recovery plants is selected only if phosphoric acid (wet process) is selected.
$Y_{11} \leq Y_{16}$	Only if the methanol plants is selected, the conventional acetic acid may be selected.

The characteristics of the superstructure were shown in Table 5-19. The superstructure has 505 continuous variables, 8 integer variables, and 416 equality constraints that describe material and energy balances for the plants. Also, there are 41 inequality constraints that describe availability of raw materials, demand for products, capacities of the plants, and logical relations in the chemical complex. The degrees of freedom are 89, and the optimal solution obtained with the Chemical Complex Analysis System is discussed below.

Table 5-19 Superstructure Characteristics (Extension 2)

- 416 equality constraints that describe material and energy balances for the plants
- 41 inequality constraints that describe availability of raw materials, demand for product, capacities of the plants, and logical relations in the chemical complex
- 505 continuous variables
- 8 integer variables
- 89 degrees of freedom

The optimal structure from the superstructure is shown in Figure 5.6, and a convenient way to show the new plants in the optimal structure is given in Table 5-20. The new acetic acid process replaced the commercial acetic acid plant in the chemical complex. A table showing the flow rates of all streams among the plants in the optimal structure is given in Appendix D.

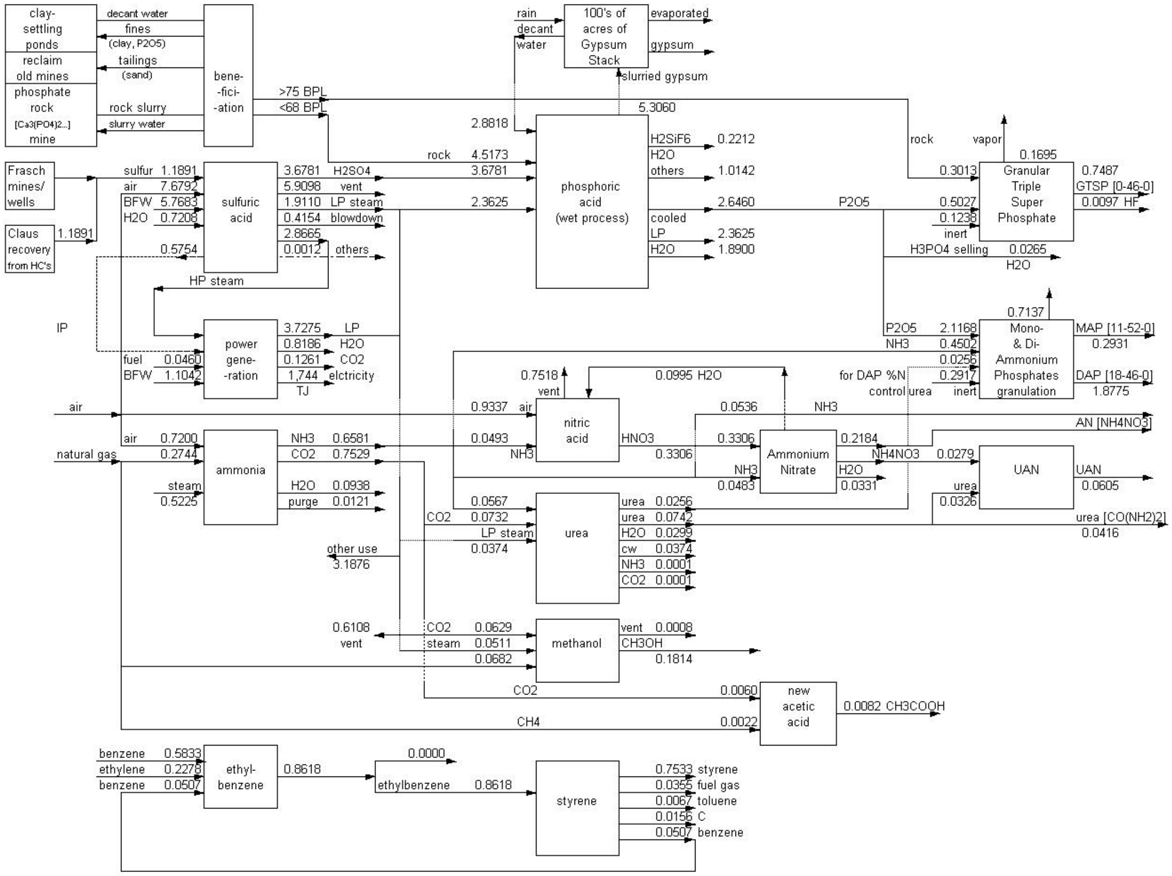


Figure 5.6 Optimal Configuration of the Chemical Production Complex, Flow Rates Million Metric Tons Per Year (Extension 2)

Comparison of the sales and costs associated with the triple bottom line, Equation 5-2, are shown in Table 5-21 for the base case and the optimal structure. The triple bottom line increased from \$343 to \$345 million per year or about 0.6% from the base case to the optimal structure. Sales increased from additional products from carbon dioxide, and there were corresponding increases in the other costs associated with producing these products by the companies. Cost to society improved since sustainable costs decreased as shown in Table 5-21 from the credits given for using carbon dioxide and increased energy efficiency.

The increased use of carbon dioxide is shown in Table 5-22 for the optimal structure. However, it was not optimal to consume all of the carbon dioxide available, and 0.61 million metric tons per year is vented to the atmosphere.

Table 5-20 Plants in the Optimal Structure from the Superstructure (Extension 2)

Existing Plants in the Optimal Structure	New Plants in the Optimal Structure
Ammonia Nitric acid Ammonium nitrate Urea UAN Methanol Granular triple super phosphate (GTSP) MAP and DAP Contact process for Sulfuric acid Wet process for phosphoric acid Ethylbenzene Styrene Power generation	Acetic acid – new process
Existing Plants Not in the Optimal Structure	New Plants Not in the Optimal Structure
Acetic acid	Electric furnace process for phosphoric acid Haifa process for phosphoric acid SO_2 recovery from gypsum waste S and SO_2 recovery from gypsum waste

Table 5-21 Sales and Costs Associated with the Triple Bottom Line for the Base Case and Optimal Structure (Extension 2)

	Base Case million dollars/year	Optimal Structure million dollars/year
Income from Sales	1,277	1,278
Economic Costs (Raw Materials and Utilities)	554	554
Raw Material Costs	542	543
Utility Costs	12	11
Environmental Cost (67% of Raw Material Cost)	362	362
Sustainable Credits (+)/Costs (-)	-18.03	-17.98
Triple Bottom Line	343	345

Table 5-22 Carbon Dioxide Consumption in Bases Case and Optimal Structure (Extension 2)

	Base Case Million metric tons/year	Optimal Structure million metric tons/year
CO_2 produced by NH_3 plant	0.75	0.75
CO_2 consumed by methanol, urea and other plants	0.141	0.142
CO_2 vented to atmosphere	0.61	0.61

In Table 5-23, the optimal capacities are given for the plants in the optimum structure of the chemical production complex. Also shown in this table is the energy used or produced for each process and the total energy required for the complex. With the new acetic acid replacing the conventional one in the optimal structure the energy required decreased from 2,150 to 1,889 TJ/year. This is reflected in the decreased utility cost shown in Table 5-21 going from \$12 to \$11 million per year. As shown in Table 5-23 the sulfuric acid plant is an important source of energy as steam, and operating this plant for steam production is as important as production of sulfuric acid.

Table 5-23 Comparison of Capacities for the Base Case and Optimal Structure (Extension 2)

Plant name	Capacity (upper-lower bounds) (mt/year)	Base Case Capacity (mt/year)	Energy Requirement (TJ/year)	Optimal Capacity (mt/year)	Energy Requirement (TJ/year)
Ammonia	329,000-658,000	658,000	3,820	658,000	3,820
Nitric acid	89,000-178,000	178,000	-775	178,000	-775
Ammonium nitrate	113,000-227,000	227,000	229	227,000	229
Urea	49,900-99,800	99,800	128	99,800	128
Methanol	91,000-181,000	181,000	2,165	181,000	2,165
UAN	30,000-60,000	60,000	0	60,000	0
MAP	146,000-293,000	293,000		293,000	
DAP	939,000-1,880,000	1,880,000	1,901	1,880,000	1,901
GTSP	374,000-749,000	749,000	1,312	749,000	1,312

Table 5-23 Continued

Plant name	Capacity (upper-lower bounds) (mt/year)	Base Case Capacity (mt/year)	Energy Requirement (TJ/year)	Optimal Capacity (mt/year)	Energy Requirement (TJ/year)
Sulfuric acid	1,810,000-3,620,000	3,620,000	-14,642	3,620,000	-14,642
Wet process phosphoric acid	635,000-1,270,000	1,270,000	5,181	1,270,000	5,181
Ethylbenzene	431,000-862,000	862,000	-755	862,000	-755
Styrene	386,000-771,000	753,000	3,318	753,000	3,318
Acetic acid	4,080-8,160	8,160	268	0	0
Electric furnace phosphoric acid	635,000-1,270,000	na	na	0	0
Haifa phosphoric acid	635,000-1,270,000	na	na	0	0
New Acetic acid	4,090-8,180	na	na	8,180	8
SO_2 recovery from gypsum	987,000-1,970,000	na	na	0	0
S and SO_2 recovery from gypsum	494,000-988,000	na	na	0	0
Ammonia sale		53,600		53,600	
Ammonium Nitrate sale		218,000		218,000	
Urea sale		41,600		41,600	
Wet process phosphoric acid sale		12,700		12,700	
Ethylbenzene sale		0		0	
CO_2 vented		612,000		611,000	
Total energy requirement			2,150		1,889

C-2. Extension of Chemical Production Complex for Agricultural Chemical Complex

One additional evaluation has been performed using GAMS, which is called the base case of Extension 3 (Figure 5.7). This extension is based on the agricultural chemical complex with the additional conventional acetic acid, sylvinite process for KCl, solid blend and liquid blend. There are fourteen production units plus associated utilities for power, steam and cooling water and facilities for waste treatment.

The raw materials used in the base case include air, water, natural gas, sulfur, phosphate rock and sylvinite ore as shown on Figure 5.7. The products are a typical solid blend of [18% N-18% P2O5-18% K2O], a liquid blend of [9-9-9], mono- and di-ammonium phosphate (MAP and DAP), granular triple super phosphate (GTSP), urea, ammonium nitrate, and urea ammonium nitrate solution (UAN), phosphoric acid, ammonia, methanol and acetic acid. Intermediates are sulfuric acid, phosphoric acid, ammonia, nitric acid, urea, methanol and carbon dioxide. The intermediates are used to produce MAP and DAP, GTSP, urea, ammonium nitrate, UAN, and acetic acid. These fertilizer compounds are either used to make blends or sold directly shown in Figure 5.7. Their pre-blending compositions are: MAP [11-52-0], DAP [18-46-0], GTSP [0-46-0], urea (CO(NH2)2) [46-0-0], ammonium nitrate [34-0-0], and UAN [~30-0-0]. Also, potassium supplied as potassium chloride for blends is produced from sylvinite plant which does not exist in the lower Mississippi River corridor. In actual practice several blends are produced, and they would just add blending constraints to the base case.

In the base case ammonia plants produce 0.75 million metric tons/year of carbon dioxide, and methanol, urea, and acetic acid plants consume 0.14 million metric tons of carbon dioxide. This leaves a surplus of 0.61 million metric tons/year of high quality carbon dioxide, as shown in Figure 5.7. This high purity carbon dioxide is being vented to the atmosphere now. A table showing the flow rates of all streams among the plants in the base case is given in Appendix D.

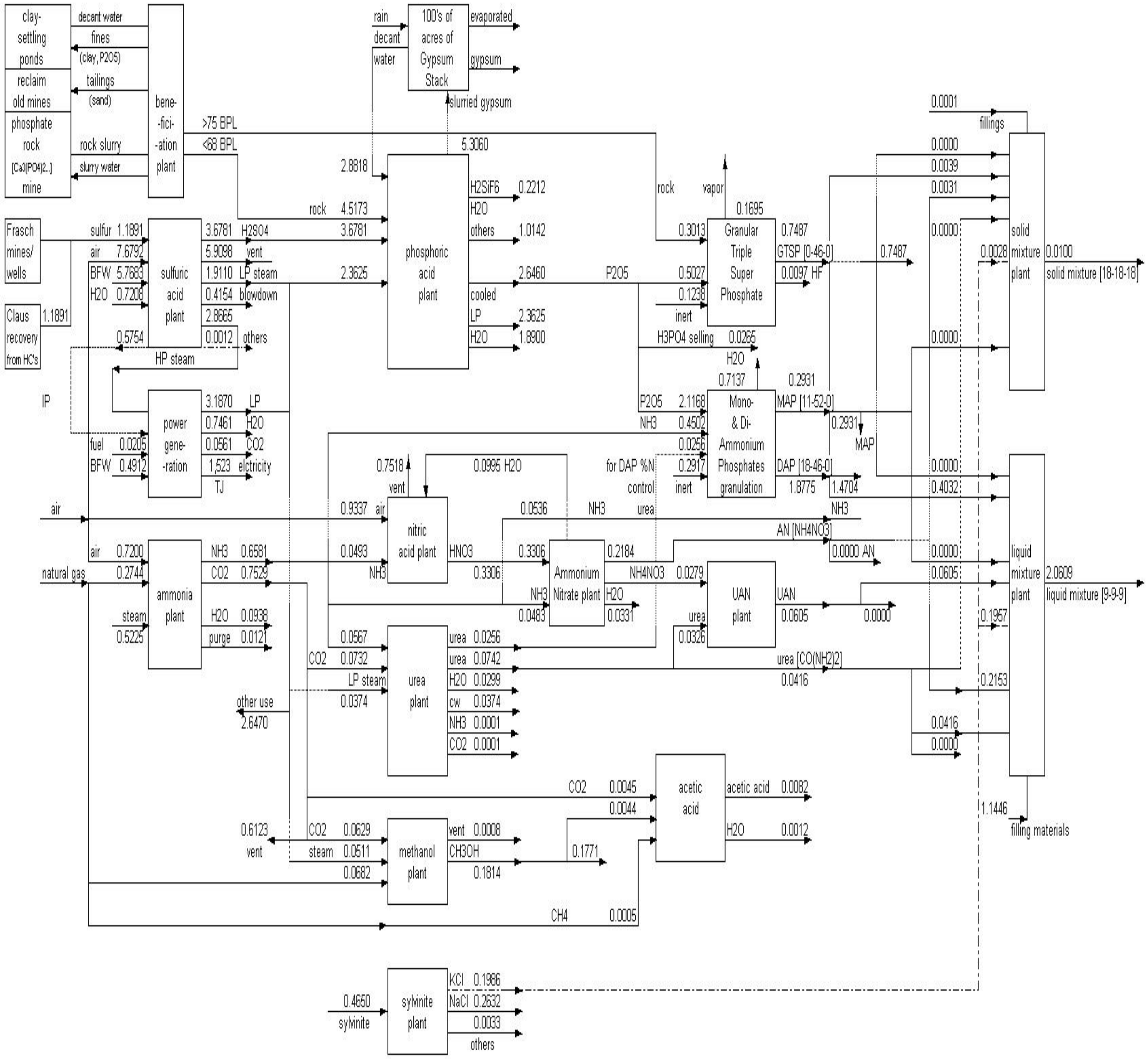


Figure 5.7 Chemical Production Complex in the Lower Mississippi River Corridor, Base Case of Extension 3, Flow Rates Million Metric Tons Per Year

The characteristics of the base case of Extension 3 are shown in Table 5-24. There are 273 equality constraints that describe material and energy balances for the plants. Also, there are 27 inequality constraints that describe the product demand, raw material availability, and capacities of plants in the chemical complex.

Table 5-24 Base Case of Extension 3 Characteristics

- 273 equality constraints that describe material and energy balances for the plants
- 27 inequality constraints that describe the product demand, availability of raw materials, and capacities of the plants in the chemical complex
- 329 of variables
- 56 of degrees of freedom

The chemical production complex shown in Figure 5.7 was expanded into a superstructure (Figure 5.8) by integrating new chemical processes for more options for the product, energy saving, and sustainable development. Two additional plants were added to produce phosphoric acid. One is the electric furnace process, which has high-energy cost but produce phosphoric acid. In the other process (Haifa process), calcium phosphate ore react with hydrochloric acid to produce phosphoric acid. Also, there are two plants that use gypsum wastes to recover sulfur and sulfur dioxide. One reduces gypsum waste to sulfur dioxide that is recycled to the sulfuric acid plant. The other reduces gypsum waste to sulfur and sulfur dioxide that are recycled to the sulfuric acid plant. Also, a new process for acetic acid production from CO_2 and CH_4 is incorporated into the superstructure. In addition, there are two more plants for KCl production. One uses brine to produce KCl, and the other uses KCl ore as

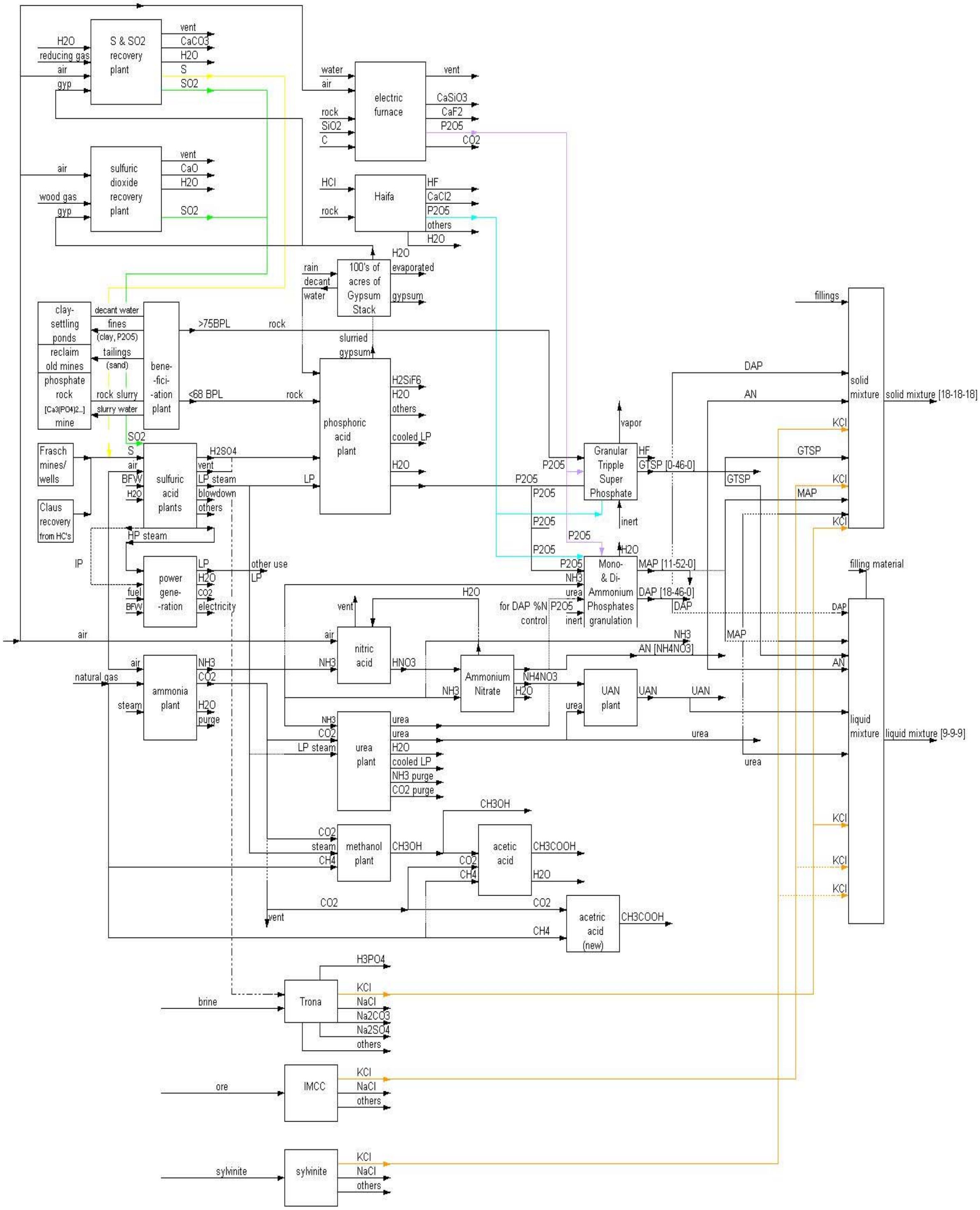


Figure 5.8 Chemical Production Complex in the Lower Mississippi River Corridor, Superstructure (Extension 3)

feedstock to produce KCl. Thus, a total of seven processes were included in the superstructure. A convenient way to show the plants in base case and the plants added to form the superstructure is given in Table 5-25. This expanded complex gives alternative ways to produce intermediates that reduce wastes and energy and consume greenhouse gases.

Table 5-25 Processes in Chemical Production Complex Base Case and Superstructure (Extension 3)

Plants in the Base Case	Plants Added to Form the Superstructure
Ammonia	Acetic acid – new process
Nitric acid	Electric furnace process for phosphoric acid
Ammonium nitrate	Haifa process for phosphoric acid
Urea	SO_2 recovery from gypsum waste
UAN	S and SO_2 recovery from gypsum waste
Methanol	Trona process for KCl
Granular triple super phosphate (GTSP)	IMC process for KCl
MAP and DAP	
Contact process for Sulfuric acid	
Wet process for phosphoric acid	
Acetic acid	
Solid blend	
Liquid blend	
Sylvinite process for KCl	
Power generation	

The sales prices for products and the costs of raw materials are given in Table 5-3 along with sustainable costs and credits, and those for the production of KCl and solid blend and liquid blend in Table 5-26. The KCl production capacities are same for all of the three production plants, upper bound 5,600,000 metric tons per year and lower bound 0 metric ton per year. Solid blend and liquid blend both only have the lower bound 10,000 metric tons per year.

Table 5-26 Raw Material Costs and Product Prices for Previous Work, Source: Constable, et al. (2000), Chemical Market Reporter, Camford Chemical Prices, Internet and C&EN (2003)

Raw Materials	Cost ($/mt)	Products	Price ($/mt)
Brine KCl	4	Phosphoric acid (Trona)	310
Searles Lake KCl ore	15	Solid blend	154
Sylvinite KCl ore	45	Liquid blend	77

Relations among the binary variables and the logical constraints used in the System are given in Table 5-27, and the binary variables associated the KCl plants are:

Trona process for KCl (Y_4)　　IMC process for KCl (Y_5)

sylvinite for KCl (Y_6)

Table 5-27 Logical Relations Used to Select the Optimal Structure (Extension 3)

Logic Expression	Logic Meaning
$Y_{11} + Y_{12} \leq 1$	At most one of these two acetic acid plants is selected.
$Y_{13} + Y_{14} \leq Y_3$	At most one of these two S and SO_2 recovery plants is selected only if phosphoric acid (wet process) is selected.
$Y_4 + Y_5 + Y_6 = 1$	Only one of the three KCl plants must be selected.

The characteristics of the superstructure were shown in Table 5-28. The superstructure has 593 continuous variables, 10 integer variables, and 481 equality constraints that describe material and energy balances for the plants. Also, there are 42 inequality constraints that describe availability of raw materials, demand for products, capacities of the plants, and logical relations in the chemical complex. The degrees of freedom are 102, and the optimal solution obtained with GAMS is discussed below.

The optimum configuration of plants was obtained from the superstructure by maximizing the triple bottom line economic model subject to the equality and inequality constraints using GAMS. The optimal structure from the superstructure is shown in Figure 5.9, and a convenient way to show the new plants in the optimal structure is given in Table 5-29. The new acetic acid process replaced the commercial acetic acid plant in the chemical complex. IMC process replaced sylvinite process for KCl production. A table showing the flow rates of all streams among the plants in the optimal structure for Extension 3 is given in Appendix D.

Table 5-28 Superstructure Characteristics (Extension 3)

- 481 equality constraints that describe material and energy balances for the plants
- 42 inequality constraints that describe availability of raw materials, demand for product, capacities of the plants, and logical relations in the chemical complex
- 583 continuous variables
- 10 integer variables
- 102 degrees of freedom

Table 5-29 Plants in the Optimal Structure from the Superstructure (Extension 3)

Existing Plants in the Optimal Structure	New Plants in the Optimal Structure
Ammonia Nitric acid Ammonium nitrate Urea UAN Methanol Granular triple super phosphate (GTSP) MAP and DAP Contact process for Sulfuric acid Wet process for phosphoric acid Solid blend Liquid blend Power generation Existing Plants Not in the Optimal Structure Sylvinite process for KCl Acetic acid	IMC process for KCl Acetic acid – new process New Plants Not in the Optimal Structure Electric furnace process for phosphoric acid Haifa process for phosphoric acid SO_2 recovery from gypsum waste S and SO_2 recovery from gypsum waste Trona process for KCl

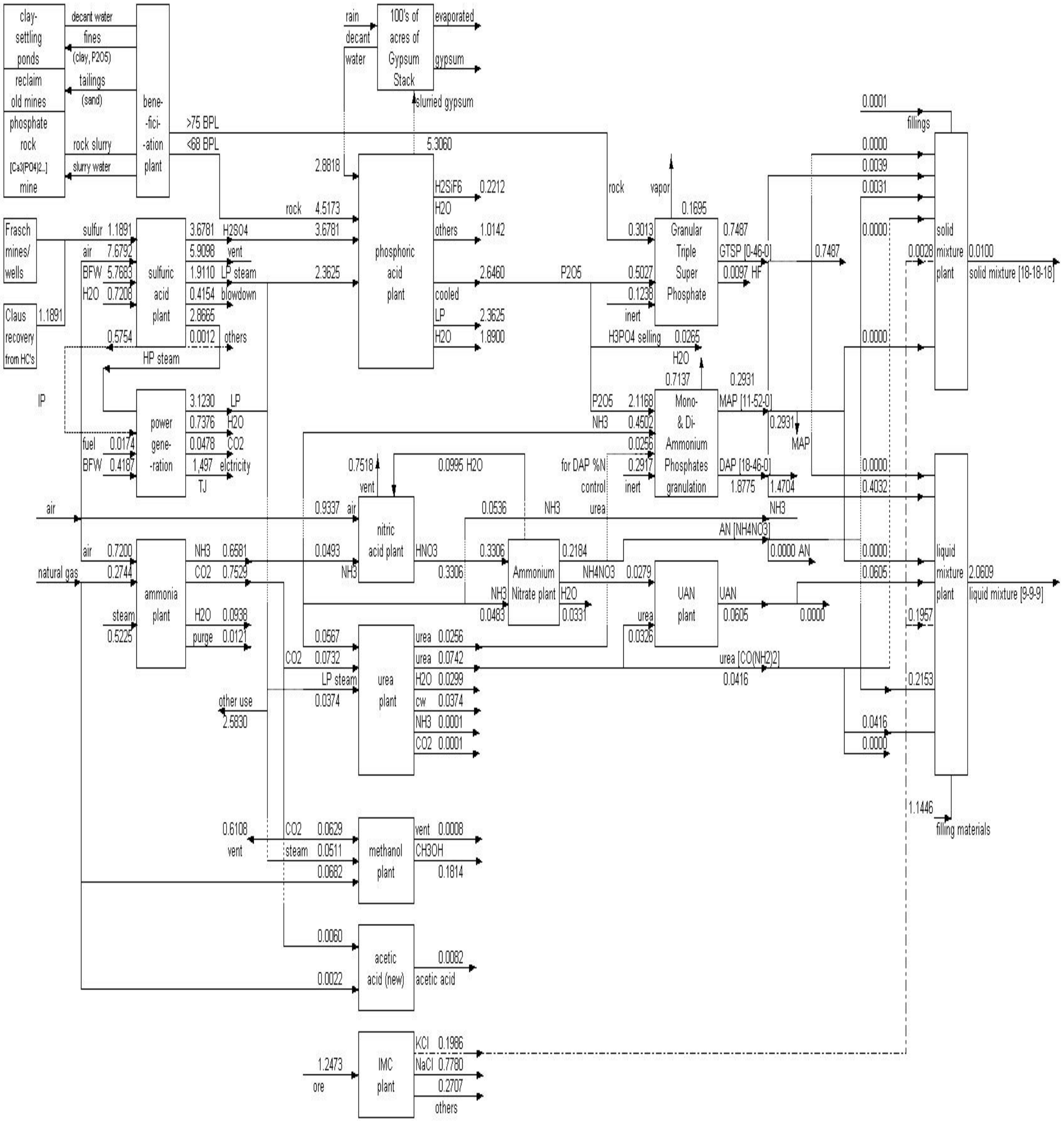


Figure 5.9 Optimal Configuration of the Chemical Production Complex, Flow Rates Million Metric Tons Per Year (Extension 3)

Comparison of the sales and costs associated with the triple bottom line, Equation 5-2, are shown in Table 5-30 for the base case and the optimal structure. The triple bottom line increased from \$199 to \$205 million per year or about 3% from the base case to the optimal structure. Sales increased from additional products from carbon dioxide, and there were corresponding decreases in the other costs associated with producing these products by the companies. Cost to society improved since sustainable costs decreased from \$17.8 to \$17.7 million per year from the credits given for using carbon dioxide and increased energy efficiency.

The increased use of carbon dioxide is shown in Table 5-31 for the optimal structure. However, it was not optimal to consume all of the carbon dioxide available, and 0.61 million metric tons per year is vented to the atmosphere.

Table 5-30 Sales and Costs Associated with the Triple Bottom Line for the Base Case and Optimal Structure (Extension 3)

	Base Case million dollars/year	Optimal Structure million dollars/year
Income from Sales	652	654
Economic Costs (Raw Materials and Utilities)	263	260
Raw Material Costs	258	256
Utility Costs	5	4
Environmental Cost (67% of Raw Material Cost)	172	171
Sustainable Credits (+)/Costs (-)	-17.8	-17.7
Triple Bottom Line	199	205

Table 5-31 Carbon Dioxide Consumption in Bases Case and Optimal Structure (Extension 3)

	Base Case million metric tons/year	Optimal Structure million metric tons/year
CO_2 produced by NH_3 plant	0.75	0.75
CO_2 consumed by methanol, urea and other plants	0.141	0.142
CO_2 vented to atmosphere	0.61	0.61

In Table 5-32, the optimal capacities are given for the plants in the optimum structure of the chemical production complex. Also shown in this table is the energy used or produced for each process and the total energy required for the complex. In the optimal structure the energy required decreased from 251 to 57 TJ/year. This is reflected in the decreased utility cost shown in Table 5-30 going from \$5 to \$4 million per year.

Table 5-32 Comparison of Capacities for the Base Case and Optimal Structure (Extension 3)

Plant name	Capacity (upper-lower bounds) (mt/year)	Base case Capacity (mt/year)	Energy Requirement (TJ/year)	Optimal Capacity (mt/year)	Energy Requirement (TJ/year)
Ammonia	329,000-658,000	658,000	3,820	658,000	3,820
Nitric acid	89,000-178,000	178,000	-775	178,000	-775
Ammonium nitrate	113,000-227,000	227,000	229	227,000	229
Urea	49,900-99,800	99,800	128	99,800	128
Methanol	91,000-181,000	181,000	2,165	181,000	2,165
UAN	30,000-60,000	60,000	0	60,000	0
MAP	146,000-293,000	293,000		293,000	
DAP	939,000-1,880,000	1,880,000	1,901	1,880,000	1,901
GTSP	374,000-749,000	749,000	1,312	749,000	1,312
Sulfuric acid	1,810,000-3,620,000	3,620,000	-14,642	3,620,000	-14,642
Wet process phosphoric acid	635,000-1,270,000	1,270,000	5,181	1,270,000	5,181
Solid blend	10,000 lower bound	10,000	0	10,000	0
Liquid blend	10,000 lower bound	2,060,000	0	2,060,000	0
Acetic acid	4,080-8,160	8,160	268	0	0
Sylvinte process KCl	0-5,600,000	198,000	664	0	0
Electric furnace phosphoric acid	635,000-1,270,000	na	na	0	0
Haifa phosphoric acid	635,000-1,270,000	na	na	0	0
New Acetic acid	4,090-8,180	na	na	8,180	8
SO_2 recovery from gypsum waste	987,000-1,970,000	na	Na	0	0

Table 5-32 Continued

Plant name	Capacity (upper-lower bounds) (mt/year)	Base case Capacity (mt/year)	Energy Requirement (TJ/year)	Optimal Capacity (mt/year)	Energy Requirement (TJ/year)
S and SO_2 recovery from gypsum waste	494,000-988,000	na	na	0	0
Trona process KCl	0-5,600,000	na	na	0	0
IMC process KCl	0-5,600,000	na	na	198,000	731
Ammonia sale		53,600		53,600	
Ammonium Nitrate sale		0		0	
Urea sale		0		0	
Wet process phosphoric acid sale		12,700		12,700	
CO_2 vented		612,000		611,000	
Total energy requirement			251		57

D. Application to the Existing Petrochemical Production Complex in the Lower Mississippi River Corridor

The Chemical Complex Analysis system also could be applied to a petrochemical production complex in the lower Mississippi River Corridor. The diagram of existing plants in the petrochemical production complex is shown in Figure 5.10. There are thirteen production units plus associated utilities for power, steam and cooling water and facilities for waste treatment, which basically are originated from ethylene, propylene and benzene. Additional information would be requested from the industrial advisors to conduct this evaluation.

The raw materials used in the petrochemical production complex include air, water, oxygen, chlorine, ammonia, ethylene, propylene, benzene, sulfuric acid, methanol, acetone, and calcium hydroxide as shown in Figure 5.10. The products include vinyl chloride monomer (VCM), ethylene dichloride (EDC), ethylene oxide

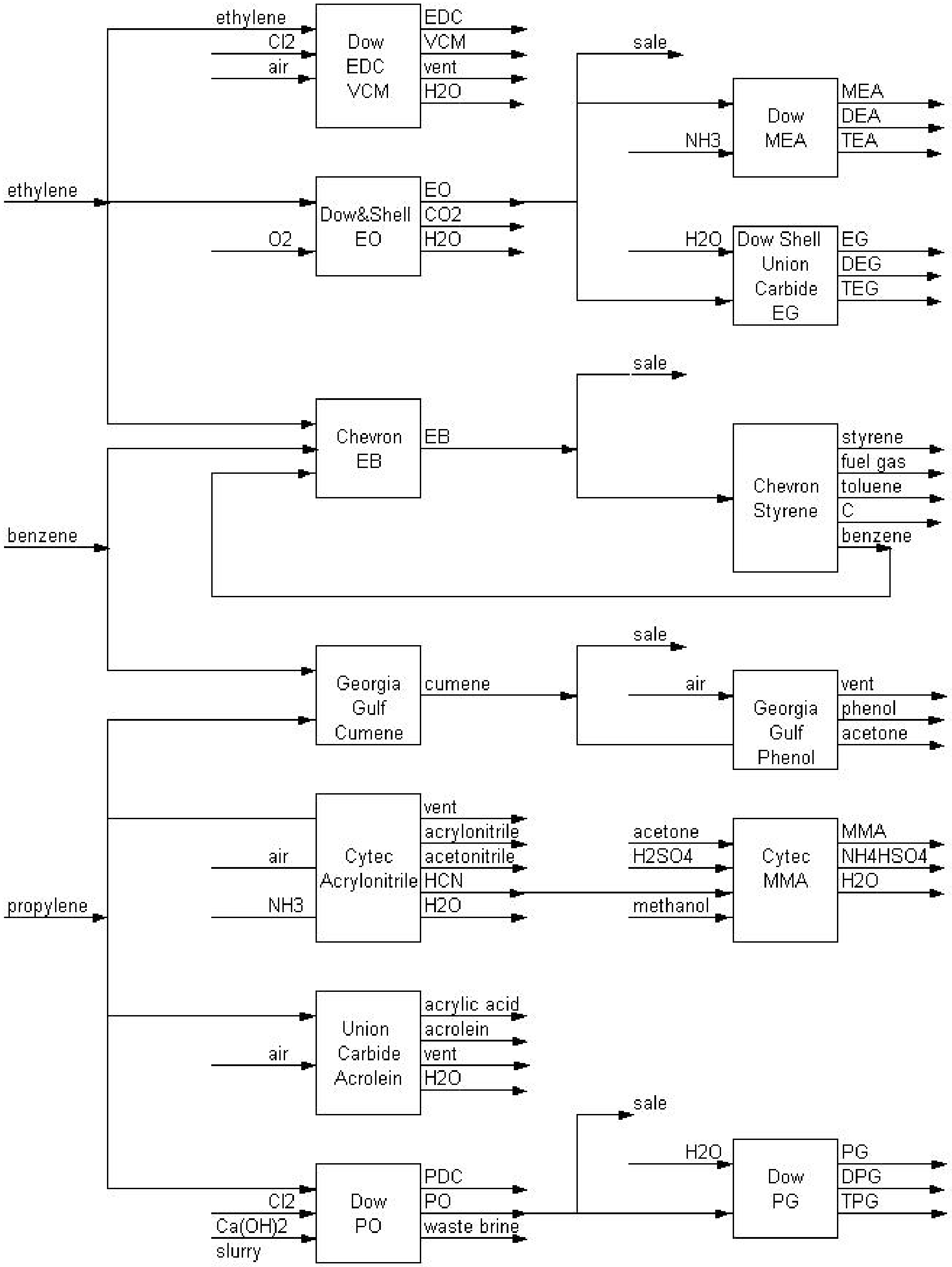


Figure 5.10 Petrochemical Production Complex in the Lower Mississippi River Corridor

(EO), ethylene glycol (EG), di-ethylene glycol (DEG), tri-ethylene glycol (TEG), mono-ethanolamine (MEA), di-ethanolamine (DEA), tri-ethanolamine (TEA), acrolein, propylene oxide (PO), propylene dichloride (PDC), propylene glycol (PG), di-propylene glycol (DPG), tri-propylene glycol (TPG), acrylonitrile, methyl methacrylate (MMA), cumene, phenol, ethylbenzene (EB) and styrene. Intermediates formed include ethylene oxide, ethylbenzene, cumene, propylene oxide and hydrogen cyanide. The intermediate ethylene oxide is used to produce MEA, DEA, TEA, EG, DEG and TEG; ethylbenzene to produce styrene; cumene to produce phenol; hydrogen cyanide to produce MMA; and propylene oxide to produce PG, DPG and TPG.

E. Comparisons with Other Investigations

There have been no other reports of research results that determined the optimization of chemical production complexes. Krotscheck and Narodoslawsky (1996) developed a Sustainable Process Index (SPI) to measure the total environmental impact of human activities of various kinds. Similarly, environmental and economic factors were incorporated together without social factors by Chen and Shonnard (2001). Meanwhile, metrics and indicators for sustainable development were developed to measure the economic, environmental and social effects of the business triple bottom line. These metrics and indicators have not been incorporated into the decision model. The external cost in power generation has been studied extensively but with a limited development and restricted only in power generation area (Rowe, et al., 1995). Eco-efficiency is one part of sustainability, dealing with economic and environmental performance in the sustainability.

TCA, LCA, eco-efficiency and sustainability metrics can be used to evaluated new products and processes (Kohlbrand, 1998). Also, modeling technology can be used to describe and predict the performance of new processes in term of traditional variables of production, product quality and efficiency but also include environmental, health safety and sustainability evaluation. There is not enough standard methodologies and measurement developed in the past two decades (Kohlbrand, 1998). Some of these tools are available individually, such as TCA, LCA, and some other being developed, for example, metrics for sustainability. SPI can be employed to tell if one process is eco-efficient or not. Also, sustainability metrics can be used to compare different independent processes (Tanzil, et al., 2002).

No one has provided the method to evaluate the sustainable development of the chemical production complex from macro-approach, which is the main task in this research. Our research develops a system for use by plant and design engineers. They can convert their company's goals and capital into viable projects that meet economic, environmental and sustainable requirements on the base of meeting the triple bottom line for business.

F. Summary

Chemical complex optimization is an effective approach for economic improvement, source reduction, and sustainable development in a chemical production complex.

The chemical production complex in the lower Mississippi River corridor has been used to show how those potentially new plants can be integrated into this existing infrastructure using the Chemical Complex Analysis System. The optimum configuration of plants was determined based on economic, environmental and sustainable costs using the System. The System was used for multicriteria optimization to find optimal solutions that maximize companies' profits and minimize costs to society, called efficient or Pareto optimal solutions. It is another decision to determine the specific value of the weight that is acceptable to all concerned. Monte Carlo simulation was used to determine the sensitivity of the optimal solution to the costs and prices for the chemical production complex triple bottom line model with the cumulative probability distribution, a curve of the probability as a function of the triple bottom line. Now a range of values is available for the optimum triple bottom line that can be used to assess the risk of proceeding as measured by the cumulative probability distribution.

Multicriteria optimization has been used with Monte Carlo simulation to determine the sensitivity of the optimal structure of a chemical production complex to prices, costs, and sustainable credits/cost. In essence, for each Pareto optimal solution, there is a cumulative probability distribution function that is the probability as a function of the triple bottom line. This information provides a quantitative assessment of the optimum profit versus sustainable credits/cost, and the risk (probability) that the triple bottom line will meet expectations.

The capabilities of the Chemical Complex Analysis System have been demonstrated by determining the optimal configuration of units based on economic, environmental and sustainable costs. Based on these results, the methodology could be applied to other chemical production complexes in the world for reduced emissions and energy savings.

CHAPTER VI CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

Based on the results of this research for chemical complex optimization, it is concluded as following:

A new method was developed to evaluate the sustainable development of a chemical production complex. A new integrated set of tools, methodology and programs was developed to perform a consistent and accurate evaluation of new plants and existing processes. A value-added model (triple bottom line) incorporated economic, environmental and sustainable costs.

A Chemical Complex Analysis System has been developed to facilitate the effort of engineers in applying chemical complex optimization. This program incorporated the detailed methodology of chemical complex optimization developed in this research project and automatically links with optimization software (GAMS) for solving the optimization problems for chemical complex optimization.

A new methodology was developed for identifying potentially new processes. Twenty potentially new processes were simulated using HYSYS and fourteen of the most promising were selected for integrating into the superstructure that includes plants in the existing chemical production complex in the lower Mississippi River corridor.

The System was developed to evaluate integrating new plants into the existing infrastructure of plants in a chemical production complex. With this system, engineers can convert company’s goals and capital into viable projects that meet economic, environmental and sustainable requirements. The System will give corporate engineering groups new capability to design energy efficient and environmentally acceptable plants and have new products from greenhouse gases.

The System was applied to and validated with an agricultural chemical complex with ten multiple plant production units in the lower Mississippi River corridor. The agricultural chemical complex was extended to a chemical production complex in the lower Mississippi River corridor for base case with existing plants. Then potentially new processes were integrated into the chemical production complex by using the System. The System determined the optimum configuration of plants based on economic, environmental and sustainable costs. The profit of the optimal structure increased by 48%, environmental costs increased by 6%, and sustainable costs decreased by 17% compared to the base case. The CO_2 vented from the ammonia plant decreased by 64%. The capabilities of the System were demonstrated to select an optimum configuration of plants in a chemical production complex incorporating economic, environmental and sustainable costs, along with considering the energy saving and CO_2 emission reduction.

Multicriteria optimization has been used with Monte Carlo simulation to determine the sensitivity of the optimal structure of a chemical production complex to prices, costs, and sustainable credits/cost. In essence, for each Pareto optimal solution, there is a cumulative probability distribution function that is the probability as a function of the triple bottom line. This information provides a quantitative assessment of the optimum profit versus sustainable credits/cost, and the risk (probability) that the triple bottom line will meet expectations.

The capabilities of the Chemical Complex Analysis System have been demonstrated for the chemical production complex in the lower Mississippi River corridor. Based on these results, the methodology could be applied to other chemical complexes in the world for reduced emissions and energy savings.

The System was developed by industry-university collaboration, and the program with users manual and tutorial can be downloaded at no cost from the LSU Mineral Processing Research Institute's website www.mpri.lsu.edu.

B. Recommendations

The following recommendations are made for future investigation in this area:

Although the methodology of chemical complex optimization is general and applicable for all chemical complexes, the plant model formulation is specific for different types of chemical processes. The plant model formulation requires extensive knowledge of the process for developing the plant model. Additional work can be focused on the software development to assist engineers to create plant models step by step. This will significantly reduce the effort of engineers in applying chemical complex optimization and avoid the errors that are possibly committed in the plant model construction.

The Pollution Index program can be applied to a chemical production complex and identifies plants that should be eliminated or modified to reduce emissions. This part of the System needs to be applied to the chemical production complex.

The superstructure can be expanded by addition of more processes that use carbon dioxide. The complex can be expanded to a petrochemical complex by adding other existing plants in the lower Mississippi River corridor. Also, processes for fullerenes and carbon nanotubes can be evaluated for inclusion in the complex.

Potential processes for fullerines and carbon nanotubes can be designed based on laboratory experimental studies that are available in the literature as were done for carbon dioxide. For example, laboratory catalytic reactors are used to produce gram quantities of carbon nanotubes, and batch purification involves removing impurities with strong mineral acids. These potentially new processes could be high temperature, energy intensive and hazardous waste generating processes. They could be designed using the Advanced Process Analysis System available from the Minerals Processing Research Institute's web site www.mpri.lsu.edu. Then these process designs could be used with the Chemical Complex Analysis System to evaluate integrating these new processes into the existing infrastructure of plants and determine the best energy-efficient and environmentally acceptable processes.

The methodology presented here can be applied to other sources of carbon dioxide. For example, flue gases from gas-fired turbines have 3.0 mol % CO_2 and coal-fired plants have 10-12% CO_2 (Freguia, et al., 2003). The standard process of amine scrubbing gives essentially pure CO_2 from flue gases, and costs range from \$50-60 per ton of CO_2 captured (Simmonds, et al., 2002). Research is described by Ondrey (2004) for new and more efficient methods to remove carbon dioxide from combustion gases.

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APPENDIX A PHYSICAL PROPERTIES OF PROCESS STREAMS

Heat capacity: $\dfrac{C_P^0(T)}{R} = a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4$ $\qquad C_P^0(T)$ unit: $J/(mol \cdot K)$

Enthalpy: $\dfrac{H^0(T)}{RT} = a_1 + \dfrac{a_2}{2} T + \dfrac{a_3}{3} T^2 + \dfrac{a_4}{4} T^3 + \dfrac{a_5}{5} T^4 + \dfrac{b_1}{T}$ $\qquad H^0(T)$ unit: J/mol

Entropy: $\dfrac{S^0(T)}{R} = a_1 \ln T + a_2 T + \dfrac{a_3}{2} T^2 + \dfrac{a_4}{3} T^3 + \dfrac{a_5}{4} T^4 + b_2$ $\qquad R = 8.3145\, J/(mol \cdot K)$

Table A-1 Coefficients of Heat Capacity and Enthalpy, from McBride, et al. (1993)

Name	Temperature (K)	a_1	a_2	a_3	a_4	a_5	b_1	b_2
Ar (g)	1000-6000	2.5000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	-7.4537E+02	4.3796E+00
	200-1000	2.5000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	-7.4538E+02	4.3797E+00
CH_4 (g)	1000-6000	1.6355E+00	1.0084E-02	-3.3692E-06	5.3496E-10	-3.1552E-14	-1.0006E+04	9.9931E+00
	200-1000	5.1499E+00	-1.3671E-02	4.9180E-05	-4.8474E-08	1.6669E-11	-1.0247E+04	-4.6413E+00
CO (g)	1000-6000	3.0485E+00	1.3517E-03	-4.8579E-07	7.8854E-11	-4.6981E-15	-1.4266E+04	6.0171E+00
	200-1000	3.5795E+00	-6.1035E-04	1.0168E-06	9.0700E-10	-9.0442E-13	-1.4344E+04	3.5084E+00
CO_2 (g)	1000-6000	4.6366E+00	2.7413E-03	-9.9583E-07	1.6037E-10	-9.1610E-15	-4.9025E+04	-1.9353E+00
	200-1000	2.3568E+00	8.9846E-03	-7.1236E-06	2.4592E-09	-1.4370E-13	-4.8372E+04	9.9010E+00
HF (g)	1000-5000	2.9919E+00	7.1489E-04	-6.8631E-08	-1.1617E-11	1.9412E-15	-3.3621E+04	3.8255E+00
	300-1000	3.4380E+00	5.3572E-04	-1.5230E-06	1.7564E-09	-5.7870E-13	-3.3819E+04	1.2062E+00
H_2O (g)	1000-6000	2.6770E+00	2.9732E-03	-7.7377E-07	9.4434E-11	-4.2690E-15	-2.9886E+04	6.8826E+00
	200-1000	4.1986E+00	-2.0364E-03	6.5204E-06	-5.4880E-09	1.7720E-12	-3.0294E+04	-8.4903E-01
H_2O (l) (c)	273.15-600	7.2558E+01	-6.6244E-01	2.5620E-03	-4.3659E-06	2.7818E-09	-4.1886E+04	-2.8828E+02
H_2 (g)	1000-6000	2.9329E+00	8.2661E-04	-1.4640E-07	1.5410E-11	-6.8880E-16	-8.1306E+02	-1.0243E+00
	200-1000	2.3443E+00	7.9805E-03	-1.9478E-05	2.0157E-08	-7.3761E-12	-9.1794E+02	6.8301E-01

Table A-1 Continued

Name	Temperature (K)	a_1	a_2	a_3	a_4	a_5	b_1	b_2
NH_3 (g)	1000-6000	2.7171E+00	5.5686E-03	-1.7689E-06	2.6742E-10	-1.5273E-14	-6.5845E+03	6.0929E+00
	200-1000	4.3018E+00	-4.7713E-03	2.1934E-05	-2.2986E-08	8.2899E-12	-6.7481E+03	-6.9064E-01
NO (g)	1000-6000	3.2607E+00	1.1910E-03	-4.2912E-07	6.9448E-11	-4.0330E-15	9.9214E+03	6.3690E+00
	200-1000	4.2186E+00	-4.6399E-03	1.1044E-05	-9.3406E-09	2.8055E-12	9.8451E+03	2.2806E+00
N_2 (g)	1000-6000	2.9526E+00	1.3970E-03	-4.9263E-07	7.8601E-11	-4.6076E-15	-9.2395E+02	5.8719E+00
	200-1000	3.5310E+00	-1.2366E-04	-5.0300E-07	2.4353E-09	-1.4088E-12	-1.0470E+03	2.9675E+00
O_2 (g)	1000-6000	3.6610E+00	6.5636E-04	-1.4115E-07	2.0580E-11	-1.2991E-15	-1.2160E+03	3.4154E+00
	200-1000	3.7824E+00	-2.9967E-03	9.8473E-06	-9.6813E-09	3.2437E-12	-1.0639E+03	3.6577E+00
S (cr)	200-368.3	3.7137E-01	1.5337E-02	-3.3544E-05	2.8925E-08	0.0000E+00	-5.5321E+02	-1.5962E+00
SO_2 (g)	1000-5000	5.2451E+00	1.9704E-03	-8.0376E-07	1.5150E-10	-1.0558E-14	-3.7558E+04	-1.0740E+00
	300-1000	3.2665E+00	5.3238E-03	6.8438E-07	-5.2810E-09	2.5590E-12	-3.6908E+04	9.6646E+00
SiO_2 (c)	200-847	-7.5851E-01	3.0577E-02	-4.0086E-05	2.1619E-08	-6.1725E-13	-1.1037E+05	1.7838E+00
$CaCO_3$ (cal) (c)	1000-1200	1.4439E+01	-1.3978E-03	2.0433E-06	0.0000E+00	0.0000E+00	-1.5040E+05	-7.2844E+01
	298.15-1000	-1.7697E+00	6.1888E-02	-8.8238E-05	4.6191E-08	-2.9873E-12	-1.4669E+05	6.3241E+00
H_2SO_4 (l) (c)	1000	9.9422E+00	2.1786E-02	3.4974E-06	-3.3549E-09	1.1700E-12	-1.0186E+05	-4.4399E+01
	300-1000	9.9422E+00	2.1786E-02	3.4974E-06	-3.3549E-09	1.1700E-12	-1.0186E+05	-4.4399E+01
C (c)	1000-5000	1.4557E+00	1.7170E-03	-6.9756E-07	1.3528E-10	-9.6759E-15	-6.9514E+02	-8.5258E+00
	200-1000	-3.1087E-01	4.4035E-03	1.9039E-06	-6.3855E-09	2.9896E-12	-1.0865E+02	1.1138E+00
$CaCl_2$ (c)	1000-1045	8.7332E+00	2.3955E-04	9.4467E-07	4.5852E-10	-5.9750E-14	-9.8308E+04	-3.7237E+01
	300-1000	6.3555E+00	1.3784E-02	-2.4421E-05	1.9551E-08	-4.9534E-12	-9.8042E+04	-2.6814E+01
CaO (s)	1000-3200	5.6558E+00	1.0165E-03	-2.5577E-07	5.4514E-11	-4.2580E-15	-7.8238E+04	-2.8223E+01
	300-1000	1.6938E+00	1.8150E-02	-2.8373E-05	2.0514E-08	-5.5176E-12	-7.7483E+04	-9.3710E+00
KCl (s)	1000-1044	3.9157E+00	-2.0927E-03	4.7310E-06	7.0152E-09	-5.5146E-12	-5.2747E+04	-1.0145E+01
	300-1000	5.3934E+00	2.6535E-03	9.6076E-07	-5.0252E-09	4.0721E-12	-5.4248E+04	-2.1597E+01

Table A-1 Continued

Name	Temperature (K)	a_1	a_2	a_3	a_4	a_5	b_1	b_2
NaCl (s)	1000-1073	2.2135E+00	1.5860E-03	5.0486E-06	2.6020E-09	-3.6487E-12	-4.9263E+04	-2.6026E+00
	300-1000	5.0241E+00	5.1949E-03	-7.2834E-06	6.0672E-09	-1.2013E-12	-5.1123E+04	-2.1227E+01
$MgCl_2$ (s)	300-987	5.4491E+00	1.6745E-02	-2.5957E-05	1.9112E-08	-5.1059E-12	-7.9344E+04	-2.4261E+01
C_2H_4 (g)	1000-6000	3.9918E+00	1.0483E-02	-3.7172E-06	5.9463E-10	-3.5363E-14	4.2686E+03	-2.6905E-01
	200-1000	3.9592E+00	-7.5705E-03	5.7099E-05	-6.9159E-08	2.6988E-11	5.0898E+03	4.0973E+00
C_3H_6(g)	1000-6000	6.0387E+00	1.6296E-02	-5.8213E-06	9.3594E-10	-5.5860E-14	-7.7660E+02	-8.4382E+00
	200-1000	3.8346E+00	3.2908E-03	5.0523E-05	-6.6625E-08	2.6371E-11	7.5384E+02	7.5341E+00
C_6H_6 (l)	278.68-500	6.3669E+01	-6.0053E-01	2.6679E-03	-5.0631E-06	3.6396E-09	-1.6708E+03	-2.4389E+02
C_3H_8(g)	1000-6000	6.6679E+00	2.0612E-02	-7.3655E-06	1.1844E-09	-7.0695E-14	-1.6275E+04	-1.3186E+01
	200-1000	4.2110E+00	1.7160E-03	7.0618E-05	-9.1959E-08	3.6442E-11	-1.4381E+04	5.6093E+00
DME(g)	200-1000	5.3056E+00	-2.1425E-03	5.3087E-05	-6.2315E-08	2.3073E-11	-2.3987E+04	7.1326E-01
	1000-6000	5.6484E+00	1.6338E-02	-5.8680E-06	9.4684E-10	-5.6650E-14	-2.5107E+04	-5.9626E+00
C_2H_6 (g)	200-1000	4.2914E+00	-5.5015E-03	5.9944E-05	-7.0847E-08	2.6868E-11	-1.1522E+04	2.6668E+00
	1000-6000	4.0467E+00	1.5354E-02	-5.4704E-06	8.7783E-10	-5.2317E-14	-1.2447E+04	-9.6868E-01

APPENDIX B STREAM DESIGNATION AND DEFINITON

Table B-1 Stream Designation and Definition in the Base Case

Name of Streams	Description
Sulfuric acid	
S2	S from Frasch mines/wells to sulfuric acid process (SAP)
S3	S from Claus recovery to SAP
S4	Total S to SAP
S7	Dry air to SAP
$S61_S$	Boiler feed water (BFW) to SAP
S66	Process water to SAP
S14	H_2SO_4 solution produced from SAP
S15	Vent gases exiting from SAP
$S16_S$	Low pressure steam (LP) (40 psig) exiting from SAP
$S17_S$	High pressure steam (HP) (600 psig) exiting from SAP
$S67_S$	Boiler blowdown H_2O from SAP
$S77_S$	Intermediate pressure steam (IP) (150 psig) exiting from SAP
S803	Impurity of sulfur from SAP
Phosphoric acid	
S13	Phosphate rock slurry to phosphoric acid plant (PAP)
S21	Gypsum stack decant water to PAP
$S24_S$	LP steam to PAP
S14	Sulfuric acid to PAP
S22	Slurried gypsum produced from PAP
S49	H_2SiF_6 solution produced from fluorides scrubbers in PAP
S50	Other inert materials in the phosphate rock from PAP
S60	Total phosphoric acid produced in PAP
$S75_S$	Condensate water from LP input in PAP
S420	Water evaporated from digestion and filtration in PAP
Granular triple super phosphate (GTSP)	
S12	Phosphate rock to GTSP
S39	Wet process phosphorous acid to GTSP
S74	Inert impurity to GTSP
S51	GTSP produced from GTSP
S63	HF produced from GTSP
S422	Water evaporated from GTSP
Ammonia	
S9	Air to ammonia plant
S10	Natural gas to ammonia plant
S68	Steam (reactant) to ammonia plant
S19	Total production of ammonia from ammonia plant
S20	Total production of CO_2 from ammonia plant

Table B-1 Continued

Name of Streams	Description
Ammonia (Continued)	
S69	Water from ammonia plant
S70	Purge from ammonia plant
Nitric acid	
S8	Air to nitric acid plant
S29	Ammonia to nitric acid plant
S71	Water from ammonium nitrate plant to nitric acid plant
S45	Nitric acid solution produced from nitric acid plant
S81	Vent gases from nitric acid plant
Urea	
$S27_S$	LP steam to urea plant for heat exchange
S31	Ammonia to urea plant
S32	CO_2 to urea plant
S46	Granular urea produced from urea plant
S53	Urea solid produced from urea plant for DAP N% control
S53H2O	Water produced from urea plant
$S65_S$	Condensed water from LP steam in urea plant
S800	NH_3 emission from urea plant
S801	CO_2 emission from urea plant
Methanol	
S11	Natural gas to methanol plant
S28	Steam to methanol plant
S33	CO_2 to methanol plant
S47	Methanol produced from methanol plant
S802	Purge from methanol plant
Ammonium nitrate	
S44	Ammonia to ammonium nitrate plant
S45	Nitric acid solution to ammonium nitrate plant
S56	Granular ammonium nitrate from ammonium nitrate plant
S62	Ammonium nitrate solution from ammonium nitrate plant
S71	Water from ammonium nitrate plant to nitric acid plant
S804	Water from ammonium nitrate plant but not to nitric acid plant
MAP and DAP	
S40	Wet process phosphoric acid to MAP and DAP plant
S42	Ammonia to MAP and DAP plant
S53	Urea produced from urea plant as N-boosters to MAP and DAP plant
S55	Inert materials to MAP and DAP plant
S52	MAP produced from MAP and DAP plant
S57	DAP produced from MAP and DAP plant
S76	Water vapor from MAP and DAP plant

Table B-1 Continued

Name of Streams	Description
UAN	
S54	Granular urea to UAN plant
S62	Ammonium nitrate solution to UAN plant
S58	UAN solution produced from UAN plant
Power generation	
$S17_S$	HP steam from sulfuric acid plant
$S77_S$	IP steam from sulfuric acid plant
Sbf	Water to the package boiler
S300	Natural gas to the package boiler
Spghp1	One branch of $S17_S$ to power generator I (PGI)
Spghp2	The other branch of $S17_S$ to power generator II (PGII)
Spglp1	LP from PGI
Spglp2	LP from PGII
Spgip	Branch of $S77_S$
Sbd	Blow-down water from the package boiler
Spgc1	Condensate water from PGI
Spgc2	Condensate water from PGII
Spgihp	HP to PGI
Spgiihp	HP to PGII
Sbhp	HP produced from the package boiler
Sbhp1	One branch of HP produced from the package boiler
Sbhp2	The other branch of HP produced from the package boiler
S78	Water from power generation plant
$S18_S$	LP steam from power generation plant
S301	CO_2 emission from the boiler
Se1	electricity generated from PGI
Se2	electricity generated from PGII
Acetic acid	
S82	CO_2 to conventional acetic acid plant
S83	Natural gas to conventional acetic acid plant
S424	Methanol from methanol plant to conventional acetic acid plant
S84	Production of acetic acid from conventional acetic acid plant
S425	Water produced from conventional acetic acid plant
Ethylbenzene	
S1067	Benzene to Ethylbenzene process
S1068	Ethylene to Ethylbenzene process
S1074	Benzene recycled from Styrene process
S1069	EB produced from Ethylbenzene process

Table B-1 Continued

Name of Streams	Description
Styrene	
S1071	Ethylbenzene to conventional styrene plant
S1072	Styrene produced from conventional styrene plant
S1073	Fuel gas produced from conventional styrene plant
S1074	Benzene produced from conventional styrene plant
S1075	Toluene produced from conventional styrene plant
S1076	Carbon produced from conventional styrene plant
Others	
S5	Total air input to the base case
S6	Total natural gas input to the base case
Sapply	Steam available for the base case
S30	NH_3 from NH_3 plant to ammonium nitrate plant and for sale
S43	NH_3 for sale
SCDEM	Total impure CO_2 emissions from the base case
S59	Urea for sale
S423	Methanol for sale

Table B-2 Stream Designation and Definition Added in the Superstructure

Name of Streams	Description
Electric furnace phosphoric acid	
S109	Ore to electric furnace phosphoric acid (EFP)
S110	Sand to EFP
S165	C needed in EFP
S200	Air needed for EFP
S201	H_2O needed for EFP
S111	Production of $CaSiO_3$ from EFP
S112	Production of H_3PO_4 from EFP
S151	Vent gas from EFP
S166	CO_2 produced from C in EFP
S202	CaF_2 produced from EFP
S203	Inert impurity in the ore separated in EFP
Haifa process phosphoric acid	
S85	Phosphate rock to Haifa process
S86	HCl solution to Haifa process
S87	Product H_3PO_4 from Haifa process
S88	Production of $CaCl_2$ in Haifa process
S152	Production of inert impurities from Haifa process
S164	Production of HF from Haifa process

Table B-2 Continued

Name of Streams	Description
Haifa process phosphoric acid (Continued)	
S205	Production of water from Haifa process
SO_2 recovery from gypsum waste	
S400	Gypsum to sulfur dioxide recovery plant
S401	Wood gas to sulfur dioxide recovery plant
S402	Air to sulfur dioxide recovery plant
S403	Vent gas from sulfur dioxide recovery plant
S404	CaO produced from sulfur dioxide recovery plant
S405	SO_2 produced from sulfur dioxide recovery plant
S406	Water produced from sulfur dioxide recovery plant
S and SO_2 recovery from gypsum waste	
S407	Reducing gas to sulfur and sulfur dioxide recovery plant
S408	Gypsum to sulfur and sulfur dioxide recovery plant
S409	H_2O to sulfur and sulfur dioxide recovery plant
S410	Air to sulfur and sulfur dioxide recovery plant
S411	SO_2 generated from sulfur and sulfur dioxide recovery plant
S412	Sulfur generated from sulfur and sulfur dioxide recovery plant
S413	Vent generated from sulfur and sulfur dioxide recovery plant
S414	$CaCO_3$ generated from sulfur and sulfur dioxide recovery plant
S415	H_2O generated from sulfur and sulfur dioxide recovery plant
New acetic acid	
S700	CO_2 to new acetic acid plant
S701	Natural gas to new acetic acid plant
S702	Production of acetic acid from new acetic acid plant
New styrene	
S971	Ethylbenzene to new styrene process
S972	Carbon dioxide to new styrene process
S973	Carbon monoxide produced from new styrene process
S974	Styrene produced from new styrene process
S975	Water produced from new styrene plant
New methanol (Bonivardi)	
S958	CO_2 to new methanol (Bonivardi) process
S959	H_2 to new methanol (Bonivardi) process
S960	CO produced from new methanol (Bonivardi) process
S961	Methanol produced from new methanol (Bonivardi) process
S962	Water produced from new methanol (Bonivardi) process
New methanol (Jun)	
S953	CO_2 to new methanol (Jun) process
S954	H_2 to new methanol (Jun) process
S955	Methanol produced from new methanol (Jun) process

Table B-2 Continued

Name of Streams	Description
New methanol (Jun)	
S956	DME produced from new methanol (Jun) process
S957	Water produced from new methanol (Jun) process
New methanol (Nerlov)	
S963	CO_2 to new methanol (Nerlov) process
S964	H_2 to new methanol (Nerlov) process
S965	Methanol produced from new methanol (Nerlov) process
S966	Water produced from new methanol (Nerlov) process
New methanol (Ushikoshi)	
S967	CO_2 to new methanol (Ushikoshi) process
S968	H_2 to new methanol (Ushikoshi) process
S969	Methanol produced from new methanol (Ushikoshi) process
S970	Water produced from new methanol (Ushikoshi) process
S990	CO produced from new methanol (Ushikoshi) process
New formic acid	
S942	CO_2 to new formic acid process
S943	H_2 to new formic acid process
S944	Formic acid produced from new formic acid process
New methylamines	
S946	CO_2 to new methylamines process
S947	H_2 to new methylamines process
S948	NH_3 to new methylamines process
S949	CO and CO_2 mixture gas produced from new methylamines process
S950	MMA produced from new methylamines process
S951	DMA produced from new methylamines process
S952	Water produced from new methylamines process
New ethanol	
S980	CO_2 to new ethanol process
S981	H_2 to new ethanol process
S982	Ethanol solution produced from new ethanol process
S983	Water produced from new ethanol process
New dimethyl ether (DME)	
S984	CO_2 to new DME process
S985	H_2 to new DME process
S986	CO produced from new DME process
S987	DME produced from new DME process
S988	Methanol produced from new DME process
S989	Water produced from new DME process
New graphite	
S992	CH_4 to new graphite process

Table B-2 Continued

Name of Streams	Description
New graphite	
S993	CO_2 to new graphite process
S994	H_2 produced from new graphite process
S995	Graphite produced from new graphite process
S996	Water produced from new graphite process
New hydrogen	
S934	CH_4 to new hydrogen process
S935	CO_2 to new hydrogen process
S936	H_2 produced from new hydrogen process
S937	CO produced from new hydrogen process
New propylene from CO_2	
S911	Propane to new propylene from CO_2 process
S912	CO_2 to new propylene from CO_2 process
S913	CO produced from new propylene from CO_2 process
S914	Propylene produced from new propylene from CO_2 process
S915	Water produced from new propylene from CO_2 process
S916	H_2 produced from new propylene from CO_2 process
New propylene	
S917	Propane to new propylene process
S918	H_2 produced from new propylene process
S919	Propylene produced from new propylene process
Sulfuric acid (Superstructure)	
S2	S from Frasch mines/wells to sulfuric acid process (SAP)
S3	S from Claus recovery to SAP
S4	Total S to SAP
S7	Dry air to SAP
$S61_S$	Boiler feed water (BFW) to SAP
S66	Process water to SAP
S405	SO_2 from sulfuric dioxide recovery process
S411	SO_2 from sulfur and sulfur dioxide recovery process
S412	S from sulfur and sulfur dioxide recovery process
S14	H_2SO_4 solution produced from SAP
S15	Vent gases exiting from SAP
$S16_S$	Low pressure steam (LP) (40 psig) exiting from SAP
$S17_S$	High pressure steam (HP) (600 psig) exiting from SAP
$S67_S$	Boiler blowdown H_2O from SAP
$S77_S$	Intermediate pressure steam (IP) (150 psig) exiting from SAP
S803	Impurity of sulfur from SAP
Granular triple super phosphate (GTSP) (superstructure)	
S12	Phosphate rock to GTSP

Table B-2 Continued

Name of Streams	Description
Granular triple super phosphate (GTSP) (superstructure) (Continued)	
S39	Wet process phosphorous acid to GTSP
S74	Inert impurity to GTSP
S114	Electric furnace H_3PO_4 to GTSP
S117	Haifa H_3PO_4 to GTSP
S51	GTSP produced from GTSP
S63	HF produced from GTSP
S422	Water evaporated from GTSP
MAP and DAP (superstructure)	
S40	Wet process phosphoric acid to MAP and DAP plant
S42	Ammonia to MAP and DAP plant
S53	Urea produced from urea plant as N-boosters to MAP and DAP plant
S55	Inert impurity to MAP and DAP plant
S115	Electric furnace H_3PO_4 to MAP and DAP plant
S118	H_3PO_4 produced from Haifa process to MAP and DAP plant
S52	MAP produced from MAP and DAP plant
S57	DAP produced from MAP and DAP plant
S76	Water vapor from MAP and DAP plant
Other Streams in superstructure	
S5	Total air input to the superstructure
S6	Total natural gas input to the superstructure
Sapply	Steam available for the superstructure
S30	NH_3 from NH_3 plant to ammonium nitrate plant and for sale
S43	NH_3 for sale
SCDEM	Total impure CO_2 emissions from the superstructure
S59	Urea for sale
S423	Methanol for sale

Table B-3 Stream Designation and Definition Added in the Extension 3

Name of Streams	Description
Trona process KCl	
S93	Brine to Trona plant
S94	Contact process H_2SO_4 to Trona plant
S95	Production of KCl from Trona plant
S96	Production of H_3PO_4 from Trona plant
S97	Production of NaCl from Trona plant
S98	Production of Na_2CO_3 from Trona plant
S99	Production of Na_2SO_4 from Trona plant

Table B-3 Continued

Name of Streams	Description
Trona process KCl (Continued)	
S100	Production of one branch of water from Trona plant
S421	Water evaporated from Trona plant
IMC process KCl	
S89	Ore to IMC plant
S90	Production of KCl from IMC plant
S91	Production of NaCl from IMC plant
S92	Production of other materials ($MgCl_2$ and H_2O) from IMC plant
Sylvinite process KCl	
S101	Raw material - sylvinite to Sylvinite process
S102	Production of KCl from Sylvinite process
S103	Production of NaCl from Sylvinite process
S104	Production of other materials from Sylvinite process
Solid blend	
S119	KCl from Trona to solid blend plant
S122	KCl from IMC to solid blend plant
S125	KCl from sylvinite to solid blend plant
S128	GTSP to solid blend plant
S130	MAP to solid blend plant
S132	DAP to solid blend plant
S146	Ammonium nitrate to solid blend plant
S150	Urea to solid blend plant
S170	Fillings to solid blend plant
S140	Production of solid blend mixture
Liquid blend	
S120	KCl from Trona to liquid blend plant
S123	KCl from IMC to liquid blend plant
S126	KCl from Sylvinite to liquid blend plant
S135	Ammonium nitrate to liquid blend plant
S137	UAN solution to liquid blend plant
S139	Urea to liquid blend plant
S147	GTSP to liquid blend plant
S148	MAP to liquid blend plant
S149	DAP to liquid blend plant
S163	filling materials to liquid blend plant
S141	Production of liquid blend mixture

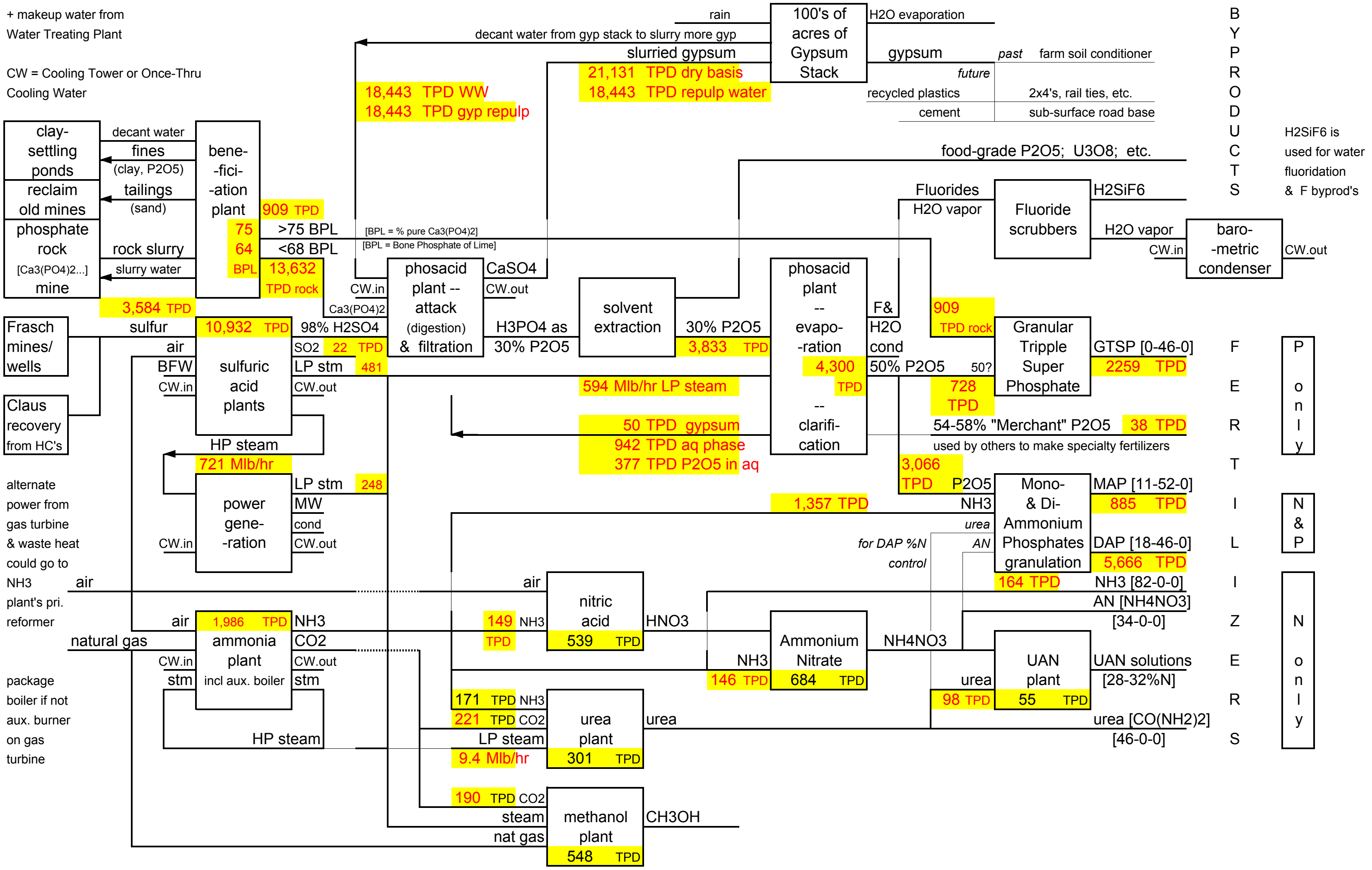
APPENDIX C INDUSTRY DATA FROM INDUSTRIAL ADVISORY GROUP

The LSU-ChE, Super-All-Options, Make-All-Possible-Products Fertilizer-Production Complex

Tom Hertwig 8/13/00

BFW = Boiler Feed Water
from condensate
+ makeup water from
Water Treating Plant

CW = Cooling Tower or Once-Thru
Cooling Water



Methanol / CH3OH / MeOH

Product purity depends on removal of hi- & lo-boilers via distillation.
Yield losses occur in:
The inerts purge that is sent to the [primary] reformer as a fuel.
Inerts include any (?? / TAH) unconverted CO2 from [process side of] reformer.
Light-end purge from product purification.
Heavy-end purge from product purification. Purge = fuel oil = ethyl, [iso-]amyl, butyl, & propyl alcohols.
Steam demand within the MeOH plant usually is a close match to the MeOH plant's steam production. (???)
Extra steam can be produced within the MeOH plant for users inside or outside the MeOH plant . . .
. . . by firing the auxilliary burners in the heat-recovery section of the exhaust gas from the primary reformer.
(TAH assumed these 3 lines were the same as in an Ammonia plant. ok??)

given
by user:

3x	CH4 + H2O -(catalyst & heat)-> CO + 3H2	**1. Steam reforming** waste heat is recovered as HP steam.
+1x	CO2 + H2 -(cat...)-> CO + H2O	**2. Water-gas shift** reaction run in reverse of what is done in an NH3 plant.
=	3 CH4 + 2 H2O + CO2 ---> 4 CO + 8 H2	**1+2. Net reaction** gives the 1:2 CO:H2 ratio needed for:
	CO + 2H2 --> CH3OH	**3. Methanol synthesis converter**

~adiabatic reactor design generates significant amounts of HP steam.
~isothermal reactor design generates no steam but (probably / TAH) uses less catalyst & less recycle.
hi- & lo-boiling impurities are removed in 2 distillation columns.

material balances:

3x	CH4 + H2O --> CO + 3H2	MW's = 16 + 18 = 28 + 3x2 = 34	1. steam reforming
+1x	CO2 + H2 --> CO + H2O	MW's = 44 + 2 = 28 + 18 = 46	2. water-gas shift
=	3 CH4 + 2 H2O + CO2 --> 4 CO + 8 H2	MW's = 3x16 + 2x18 + 44 = 4x28 + 8x2 = 12	1+2.
+4x	CO + 2H2 --> CH3OH	MW's = 28 + 2x2 = 32	3. Methanol synthesis converter
=	3 CH4 + 2 H2O + CO2 --> 4 CH3OH	MW's = 3x16 + 2x18 + 44 = 4x32 = 128	1+2+3.

	1 year	365.25	357.95	days basis
	0.98			stream factor (99?+% outside of major overhauls) (not used in any calculation yet)
	200,000	548	559	Methanol production, TPY, TPD, & TPD-up (typical plant capacity = ___ TPD)
	0.999		TAH WAG	overall H2 utilization
	0.990		TAH WAG	overall CO2 utilization

stoichiometric flows, TPD:

Syngas loop C/H ratio set point may not be exactly 1:2.00 . . . but I'll assume 2.00 for now. / TAH

	75,075	206	210	CH4 requirements, TPY, TPD, & TPD-up
	69,444	190	194	CO2 requirements, TPY, TPD, & TPD-up
add 7/21/0	28	0.08	0.08	H2 purged, TPD & TPD-up
131	new 6/2/04	0.36	0.37	CO purged, TPD & TPD-up
	694	1.90	1.94	CO2 purged, TPD & TPD-up
		1 :	0.69	C/H mole ratio in purge

energy info based on NH3 plant relationships (valid??) & MeOH plant CH4 consumption

	35	unit energy consumption, nat gas & steam (27-45 GJ / metric ton NH3 produced based on Shreve p309)
17,386		total energy consumption, nat gas & steam, GJ / D
16,486	30.11	total energy consumption, nat gas & steam, MMbtu / D & MMbtu / T NH3 (1 btu = 1054.6 joules)
9,809	17.91	process CH4, MMbtu / D & MMBtu / T (higher heating value)
8,839	16.14	process CH4, MMbtu / D & MMBtu / T (lower heating value)
7,647	13.97	balance of energy usage (based on LHV [what was assumed by Shreve?])
		fuel CH4 to heat reformer (partially recovered as steam)
f(plt stm bal)		fuel CH4 to auxilliary burners (exist ???) to make more HP steam
2,190	4.0	steam production [&? usage], TPD & T/T, includes steam used by the NH3 plant (typically 4 per Shreve p307)
5,257	9.60	steam production [&? usage], MMBtu / D (usage usually matches production / tah)

this assumes ~200oF superheat to get ~1200 Btu/lb to condense.

Nitric Acid / HNO3(aq)

NH3(g) + 2O2(g) --> HNO3(aq) + H2O(l)
MW's = 17.03 + 2x32.00 = 63.02 + 18.016 = 81.03
O2 = 20.946% of air

commercial grades range o.534-o.687 w/w (36-42^{o}Be)
concentrating to o.95 is possible with additional processing cost . . .
. . . for extractive distillation w/ a dehydrating agent as H2SO4 w/ MgSO4. Shreve p314
manufactured acid contains some HNO2 when o.20-o.45 HNO3.
manufactured acid contains dissolved N2O4 when >o.55 HNO3.

atmospheric-pressure plants are no longer used -- too big/expensive & limited to max. o.50-o.55 HNO3.
single-pressure / American / DuPont plants have lower capital cost and produce more by-product steam than:
dual-pressure / European plants that have lower catalyst cost and slightly higher yield. Shreve p315
overall costs are so\imilar for single- vs dual-pressure processes.

	1 year	365.25	357.95	days basis	
	0.98			HNO3 stream factor	
		539		NHO3 to AmNO3 production, TPD	
	0	0		HNO3 sales, TPY & TPD	
	196,814	539	550	HNO3 production, TPY, TPD, & TPD-up (100% HNO3 basis) (typical plant capacity = 225 TPD / Shreve p316)	
		0.54		product concentration (o.54-o.68)	
	364,471	998	1018	HNO3 production, as solution TPY, TPD, & TPD-up	tonnage-wise, its easier
rev 6/2/04	54,271	149	152	process NH3 requirements, TPD & TPD-up (excl. stack control)	to ship NH3 than HNO3
		558	570	O2 requirements to burn NH3, TPD & TPD-up	
	7/21/04	2,414	2,463	equivalent air requirements, TPD & TPD-up (TAH assumes excess is needed)	
		426	435	air requirements to "bleach" red NO2 out of product HNO3, TPD & TPD-up (Shreve p317)	
		157	160	water generated by burning NH3, TPD & TPD-up	
		302	308	makeup water needed for spec'd product concentration, TPD & TPD-up	
				assume NH3 is 100% burned to NO(x)	
		0.980		NO absorption (o.97-o.98)	
		0.998		NO absorption legal min. (o.998)	
		0.52	0.54	legal NO emissions, TPD & TPD-up	
		4.72	4.82	NO emissions requiring treatment, TPD & TPD-up	

treatment = stack gas is reheated & CH4, NH3, or H2 is added to reduce NO to N2.
CH4 requirement (get significant temp rise & energy recovery in process gas expander)
NH3 requirement (need catalyst; get small temp rise)
H2 requirement (need catalyst; get small temp rise)
or add a 5^{o}C section to the NO absorber ($$)

oxidation catalyst is consumed mostly by erosion and is a significant operating expense.
Shreve (1984) p317-8: single & dual press = $5 & $1.50 / metric T HNO3 produced
overall reaction ΔH = -437 kJ/kg mol NH3(g) + 2O2(g) --> HNO3(aq) + H2O(l)
process air is heated in an exchanger downstream of the catalyzed NH3 oxidation.
next downstream, steam is generated, Mlb/hr & Mlb/hr-up (1140 kPa / Shreve p316)
Shreve (1984) p317-8: dual-press process recovers less steam than single-press process.
some steam may be needed to vaporize NH3 feed if that feed is liquid.
cooling water requirements for the absorber.

Ammonium Nitrate / NH4NO3 / AmNO3

NH3(g) + HNO3(aq) --> NH4NO3(aq) MW's = 17.03 + 63.02 = 80.05

ΔH = -86.2 kJ / ____ Pure AmNO3 would be (2x14.007/80.05 =) 35.00%N

both feeds are preheated & product is air-cooled.

if feeds are properly heated & proportioned, the heat of reaction finishes drying the product.

water vapors are condensed [to recover any escaping NH3 &/or NO / TAH]

condensate goes back to NO absorber in NHO3 process (process sketch in CF pamphlet)

product is prilled or granulated. . . or ?? solution for use in making UAN solution ??

1 year	365.25	357.95	days basis
0.98			AmNO3 stream factor
250,000	684	698	AmNO3 production, TPY, TPD, & TPD-up
			(typical plant capacity = ___? TPD)
	146	149	NH3 requirements, TPD & TPD-up (excl. losses)
	539	550	HNO3 requirements, TPD & TPD-up (excl. losses)
1.000			NH3 utilization
1.000			HNO3 utilization
	0.00	0.00	NH3 losses, TPD
	0.00	0.00	HNO3 losses, TPD
53,186	146	149	NH3 requirements, TPD & TPD-up (<u>incl</u>. losses)
196,814	539	550	HNO3 requirements, TPD & TPD-up (<u>incl</u>. losses)

some steam may be needed to vaporize NH3 feed if that feed is liquid.

steam is needed to preheat the 2 feeds to assure a dry product of their reaction:

NH3

HNO3

AmNO3 solution [what strength?] may be used for making UAN solution.

Urea Amonium Nitrate solutions / UAN / URAN

	1 year		365.25	DPY
	N wt	total wt		
			AmNO3 solution strength, %AmNO3	
			spec's 30	
		rev 7/21/04	minimum =	<u>%N used</u>
restored	3,224	9,211	AmNO3 feed, dry basis (35.00%N if pure)	35.0
equations	3,224	30,702	AmNO3 solution tons	
6/2/04	16,544	35,966	Urea feed (typ 46%N; 46.64%N if pure)	46.0
	20,000	66,667	UAN produced, TPY	
	55	183	UAN produced, TPD	
			UAN solution %N (commercial spec 28-32%)	30.0

Ammonia / NH_3, anhydrous

Product can be liquid or gas. Liquid provides surge capacity for storage but requires major refrigeration equipment.
When a local customer can use vapor, this saves the cost of re-vaporizing the NH_3.
Product purity is fairly high. A trace of water is added to the NH_3 liquid product to control corrosion of carbon steel.
Steam demand within the NH_3 plant usually is a close match to the NH_3 plant's steam production.
Extra steam can be produced within the NH_3 plant for users inside or outside the NH_3 plant . . .
. . . by firing the auxilliary burners in the heat-recovery section of the exhaust gas from the primary reformer.
The biggest yield losses are in the inerts purge.
Inerts include Ar from the air feed & CH_4 from the [CO_2] Methanator.
The purge is usually passed through a H_2-Recovery Unit (HRU).
Where the purge contains enough CH_4 (& H_2), the purge is sent to the primary reformer as a fuel.

$CH_4 + H_2O$ -(catalyst & heat)-> $CO + 3H_2$	**1. Steam reforming** (generates H_2 needed for NH_3 synthesis)
$CO + H_2O$ -( )-> $CO_2 + H_2$	water-gas shift reaction (incomplete here)
$CH_4 + 2H_2O$ -( )-> $CO_2 + 4H_2$	net reaction . . . when completed in shift converter
$CH_4 + 2O_2$ --> $CO_2 + 2H_2O$ + heat	**2. Secondary reformer**
?? $CO + 0.5\ O_2$ --> CO_2 + heat ??	?? Converts some CO to CO_2 ?? . . .
?? $H_2 + 0.5\ O_2$ --> H_2O ??	?? Does this reaction occur ??
	Injected air is source of N_2 needed in NH_3 synthesis.
	Reaction heat is recovered as steam to drive process equipment.
	Combination of H_2 purification & feed of purified N_2 can eliminate
	air feed & sec reformer. Cuts inerts purge & steam production.
$CO + H_2O$ -(catalyst usually)-> $CO_2 + H_2$	**3. Water-gas shift** reaction to convert last of CO
	4. Use amines to **scrub out CO_2**.
	& ?? excess water ??
$CO_2 + 4H_2$ -(cat?)-> $CH_4 + 2H_2O$	**5. Methanation** to remove last traces of CO_2.
	6. Condense out water just before going to hi-press syngas loop.
$0.5\ N_2 + 1.5\ H_2 = NH_3$	**7. NH3 synthesis**

	1 year	365.25	357.95	days basis
	0.98			stream factor (99+% outside of major overhauls) (not used in any calculation yet)
				. . . For now, all calculations below assume 100% stream factor for the Ammonia plant.
	495,502	1,357		NH_3 requirements in Phosacid Ammoniation
	62,443	171		NH_3 requirements in Urea
	54,271	149		NH_3 requirements in Nitric Acid
53,186	53,186	146		NH_3 requirements in Ammonium Nitrate
	59,985	164.23		NH_3 sales
	725,387	1,986	2,027	total NH_3 requirments, TPD (typical plant capacity = <~1600-2000? TPD)
	0.000		TAH WAG	trace of water added to NH_3 product for corrosion control (not used in any calc'n yet)
	0.999		TAH WAG	overall H_2 utilization (higher than N_2 utilization due to H_2 recovery unit)
	0.995		TAH WAG	overall N_2 utilization

material balances:

$CH_4 + 2H_2O$ --> $CO_2 + 4H_2$	MW's = 16 + 2x18 = 44 + 4x2	1. Steam Reforming
$CH_4 + 2O_2$ --> $CO_2 + 2H_2O$	MW's = 16 + 2x32 = 44 + 2x18	2. Secondary reformer
$0.5\ N_2 + 1.5\ H_2 = NH_3$	MW's = 0.5x28 + 1.5x2 = 17	7. NH3 synthesis

N_2 = 78.084% of air
O_2 = 20.946% of air
Ar = 0.934% of air
CO_2 = 0.033% of air

1 year **stoichiometric flows, year-avg TPD:**

Syngas loop H/N ratio set point may not be exactly 3.00 . . . for reasons I do not remember.
Use of HRU certainly changes the H/N ratio set point in the syngas loop feed.

		702		process CH_4 to generate H_2
		126		process CH_4 to remove O_2 as CO_2
	302,267		828	process CH_4 total
		1,644		process N_2 & air, dry basis (adjusted to control syngas loop N:H at ~3.0)
		504		O_2 with process N_2
rev 7/21/04		28		Ar with process N_2
add 7/21/04		1		CO_2 with process N_2
	794,990		2,177	process air, dry basis (adjusted to control syngas loop N:H at ~3.0)
	576,619	1,579		process steam (excess is used to drive water-gas-shift reaction to completion)
	103,481	283		H_2O produced (some of this may displace pri reformer steam addition for shift reactor reaction)
		2,276		CO_2 produced
		1		CO_2 recovered from inlet air
	831,632		2,277	CO_2 export
	725,387	1,986		NH_3 produced
	13,371	37		inerts purge, Ar, N_2, CH_4, H_2, … (fed to pri reformer as fuel gas)
		0.000		net material balance

221	CO_2 to Urea
190	CO_2 to MeOH
1,866	balance to vent

	35	unit energy consumption, nat gas & steam (27-45 GJ / metric ton NH_3 produced based on Shreve p309)
63,059		total energy consumption, nat gas & steam, GJ / D
59,794	30.11	total energy consumption, nat gas & steam, MMbtu / D & MMbtu / T NH_3 (1 btu = 1054.6 joules)
39,493	19.89	process CH_4, MMbtu / D & MMBtu / T (higher heating value)
35,588	17.92	process CH_4, MMbtu / D & MMBtu / T (lower heating value)
24,206	12.19	balance of energy usage (based on LHV [what was assumed by Shreve?])
		fuel CH_4 to heat primary reformer (partially recovered as steam)
f(plt stm bal)		fuel CH_4 to auxilliary burners to make more HP steam
7,944	4.0	steam production [&? usage], TPD & T/T, includes steam used by the NH_3 plant (typically 4 per Shreve p307)
19,066	9.60	steam production [&? usage], MMBtu / D (usage usually matches production / tah)
		this assumes ~200oF superheat to get ~1200 Btu/lb to condense.

Urea / NH2CONH2

CO2 + 2NH3 --> NH2COONH4 --> NH2CONH2 + H2O
MW's = 44.01 + 2x17.03 = 78.07 = 60.06 + 18.016

CO2 & NH3 both come from an ammonia plant.
NH3 feed is as a liquid. May??? also provide for import of NH3 as a gas. State will impact energy requirements.
Liquid NH3 provides surge between NH3 & Urea plants, but loss of CO2 shuts Urea plant down anyway.
Product used to be prilled but today it is usually granulated .
Product is relatively pure. Some of an undesirable dimer called biuret is formed - NH2CONHCONH2-2H2O
Various additives/coatings are usually used to retard decompositon.

Commercial Urea is nominally 46%N
Pure Urea would be (2x14.007/60.06 =) 46.64%N

	1 year	365.25	357.95	days basis
	0.98			Urea stream factor (no higher than NH3 plant's stream factor)
	110,000	301	307	Urea production, TPD & TPD-up (100% (NH2)2CO basis) (typical plant capacity = 700? TPD)
		171	174	NH3 requirements, TPD & TPD-up (excl. losses) (fed as liquid)
		221	225	CO2 requirements, TPD & TPD-up (excl. losses) (compressed to 14 MPa; 2200 psig)
		1,866		additional CO2 available from NH3 plant
	0.999			NH3 utilization
	0.999			CO2 utilization (using excess CO2 helps NH3 conversion & CO2 emissions are not regulated like NH3 is.)
added	62	0.17	0.17	NH3 losses, TPD in evaporator vapors; NH3 could be scrubbed with H2SO4, H3PO4?, etc.
7/21/04	81	0.22	0.23	CO2 losses, TPD
	62,443	171	174	NH3 requirements, TPD & TPD-up (incl. losses)
	80,685	221	225	CO2 requirements, TPD & TPD-up (incl. losses)
	32,996	90	92	H2O generated by reaction, TPD & TPD-up
	0.80			evaporator's steam efficiency (0.75-0.85 / TAH est.)
added	3,437	9.4	9.6	evaporator's LP steam requirements, Mlb/hr & Mlb/hr-up
7/21/04		LOW!?		
				heat of forming the intermediate Am Carbamate = ∆H = -155 MJ / kg mol
	0			much of this heat goes into steam generation in the High-Pressure [Am Carbamate] Condenser.
				enough heat is left in the product stream to drive the decomposition step in the Urea Reactor (the first-stage decomposer).
				heat of decomposing the intermediate Am Carbamate = ∆H = +42 MJ / kg mol
				heat is left over from the formation step in the High-Pressure [Am Carbamate] Condenser.
				also, steam heat [&? heat of CO2 compression?] is added in the High-Pressure Stripper . . .
				. . . where the process-feed CO2 strips unreacted NH3 & CO2 out of the Urea / Am Carbamate solution.
				the stripped NH3 & CO2 go back into the High-Pressure Condenser for reaction.
				the Am Carbamate goes forward to the Rectifying Column [=?= the "2nd-stage decomposer"].
				some air in introduced with the CO2 to minimize system corrosion.
				customer's use of urea as a solution saves evaporation costs. Solution can be used as makeup "water" in Phosacid Ammoniation.
				a solution up to 75% urea is available from the evaporator feed.
				a ~20-50% urea solution is available for export from the [??] process scrubbers.
				. . . else this solution has to be evaporated using additional steam.
				NET steam requirments based on an actual plant are roughly:
		34	24	40# steam (55 Mlb/hr for a 700 TPD plant)
		17	37	550# steam for turbines (85 Mlb/hr for a 700 TPD plant)

Sulfuric Acid / H2SO4

SO3 absorption is most complete at 98.5% H2SO4 (balance H2O) and there it is essentially complete.
Product strength minimum is 92% to minimize corrosion of carbon steel.
Product strength maximum is 99% to minimize stack opacity (incomplete SO3 absorption).
Product purity is fairly high with the biggest usual contaminants being Fe at <<50ppm.
Anodic protection of storage tanks helps reduce Fe contamination.
Other major impurities include unconverted SO2 & Ca/Na/SiO2 from the dilution water.

S + O2 --> SO2 + much heat	furnace	MW's = 32.06 + 32.0 = 64.06
SO2 + 0.5 O2 --> SO3 + heat	converter	MW's = 64.06 + 16.0 = 80.06
SO3 + H2O --> H2SO4 + heat	absorber	MW's = 80.06 + 18.02 = 98.08

	1 year	365.25	343.34	days basis
	0.94			SAP stream factor (0.90-0.99)
	3,993,070			H2SO4 requirements in Phosacid plant, TPY
	0			H2SO4 sales, TPY
	3,993,070	10,932	11,630	H2SO4 total requirements, TPY, TPD, & TPD SAP-up
				(typical plant capacity = 1800-3600 TPD)
	4.0			stack SO2 emissions, lb SO2 / T H2SO4 produced (max 4.0)
	7,986	21.86	23.26	stack SO2 emissions, TPD & TPD-up
	0.001			sulfur impurities, decimal fraction; ash & hydrocarbons
	1309161.78	3,584	3,813	sulfur requirement, TPD & TPD-up (short tons & including impurities)
	0.08			boiler blowdown as fraction of BFW feed (typ = 0.05-0.10)
	9.1			TPD H2SO4 / Mlb/hr of HP drum steam (typ = 8.5-9.7, not including IP steam)
	0.40			fraction of HP drum steam used by blower turbine (typ = 0.35-0.60)
		1,201	1,278	[HP] drum steam, Mlb/hr & Mlb/hr-up
		481	511	HP steam to blower turbine, becomes LP steam, Mlb/hr & Mlb/hr-up
		721	767	HP steam exported from SAP's, Mlb/hr & Mlb/hr-up
		1,306	1,389	Boiler Feed Water, Mlb/hr & Mlb/hr-up
		2,610	2,776	BFW, gpm & gpm-up
		104.5	111.1	blowdown, Mlb/hr & Mlb/hr-up
	0.3			fraction of SAP capacity with Heat Recovery System producing IP steam
	150			Mlb/hr IP steam from a 3400 TPD SAP with HRS
		144.7	153.9	IP steam Mlb/hr & Mlb/hr-up
	0.985			sulfuric product concentration (0.93-0.99; 0.985 minimizes stack opacity)
		2,174	2,313	dilution water required, TPD & TPD-up
		362	385	dilution water required, gpm & gpm-up
add 7/20/04	6357657.16	1,451	1,543	total boiler feed water, Mlb/hr & Mlb/hr/up (incl.IP)

Phosphoric Acid / H3PO4 or P2O5, its anhydrous form

Described is the "wet process" for phosacid production vs the much-more-expensive furnace process.
- Wet-process acid is very impure but good enough for fertilizer, a product that is spread on the ground.
- Food-grade phosphates use furnace acid or wet-process acids made from cleaner rock and cleaned up by solvent extraction, etc.

Phosphate rock is digested in H2SO4 to swap H & Ca:
- Soluble H is moved from the SO4= to the PO4≡ (PO4 must be soluble for plants to have access to it.)
- Insoluble Ca is moved from the PO4≡ to the SO4= (Ca must be insoluble to be removeable.
  - Digestion with HCl, HNO3, H3PO4, etc. would leave Ca soluble & inseparable from the phosacid.)

Digestion is controlled to promote big, filterable gypsum crystals since filtration is the rate-limiting step.
Product acid contains residual CaSO4-2H20 solids (gypsum) & in solution.
Careful control of clarification can maximize removal of CaSO4-2H2O . . .
. . . that is a significant diluant in the downstream phosphates.
Rock contains many impurities, especially F, Fe, Al, Mg, Si, . . .
- F & Si are liberated in digestion and can be recovered for byproduct sale.
- Most of the Fe, Al, & Mg remain in solution, staying with the phosacid & downstream phosphates.

Digestion product strength is typically 25-29% P2O5 (=anhydrous form of H3PO4)
Digestion product is usually evaporated to 45-55%P2O5:
- To help the water balance in Phosacid Ammoniation.
- To allow for additional purge of impurities -- CaSO4-2H2O & F (as recoverable H2SiF6)

An alternate process is the hemi-hydrate process that produces CaSO4-o.5H2O as an intermediate.
- Product is produced at ~40% P2O4 for major savings of steam that is freed up for power production.

Management of byproduct gypsum is a major envirornmental concern, mostly for its P&F contents. Radon, too.
- Gypsum is typically stacked 50-300 feet high x hundreds of acres next to the Phosacid plant.
- To minimize groundwater contamination, the ground must be lined before starting a new stack . . .
- . . . & after the stack is as high as practical, it is covered with soil & grass to minimize contamination of runoff water.
- Due to a re-crystallization step, gypsum from the hemi-hydrate process is cleaner than from the di-hydrate process, . . .
- . . . so gypsum from the hemi process can be used for wallboard, etc. with a little extra processing.

	98% H2SO4 + H2O --> 2% H2SO4	much heat of dilution
3x	Ca3(PO4)2 + 3 H2SO4 + 6 H2O --> 3 CaSO4-2H2O + 2 H3PO4	digestion (ignoring F present in rock)
+1x	CaF2 + H2SO4 + 2 H2O --> CaSO4-2H2O + 2 HF	(the F content)
=	CaF2-3Ca3(PO4)2 + 10 H2SO4 + 20 H2O --> 10 CaSO4-2H2O + 6 H3PO4 + 2 HF	digestion (including F present in rock)
	approximate compostion of phosphate rock	

3x	MW's = 310.20 + 3x98.08 + 6x18.016 = 3x172.17 + 2x98.00 = 712.5	for the
+1x	MW's = 78.08 + 98.08 + 2x18.016 = 172.17 + 2x20.0 = 212.2	3 reactions
=	MW's = 1008.68 + 10x98.08 + 20x18.016 = 10x172.17 + 6x98.00 + 2x20.0 = 2349.7	above

	1 year	365.25	332.38	days basis
	0.91			PAP stream factor (typically 0.85-0.95)
	1,400,000	3,833	4,212	30% P2O5 production, TPY, TPD, & TPD-up (typical plant capacity = 1000-1800 TPD)
new 6/29/04	0.980			fraction of P2O5 digested
	0.960			net P2O5 recovery in digestion & filtration ("net" because some P2O5 is recovered from pond water)
		159.7	175.5	P2O5 net losses in digestion & filtration, TPD & TPD-up
	64.0			rock BPL (% pure Ca3(PO4)2; BPL = Bone Phosphate of Lime; "pure" fluorapatite would be 92.3 BPL)
	3.557			T rock / T P2O5 produced
	4,979,120	13,632	14,980	rock required, TPY, TPD, & TPD-up
frac of		568	624	rock required, TPH & TPH-up
total ***				H2SO4-to-rock ratio used in digestion, T 100% H2SO4 / T 6_-BPL rock
0.82	0.661	rev 6/25/04		theoretical/stoichiometric for fluorapatite
0.03	0.021	rev 6/30/05	rev 7/21/04	theoretical to get 2.0 % SO4 in 28% P2O5
0.15	0.120			due just to presence of CaCO3 in the rock (presence is indicated by ever-present foaming in digestion)
1.00	0.802			total (typically o.75-o.85)
	3,993,070	10,932	12,014	H2SO4 requirements, TPY, TPD, & TPD PAP-up
				T gypsum produced / T P2O5 produced (some gyp goes forward with [evaporator-] product acid.):
0.99	4.13	rev 6/25/04		theoretical for fluorapatite
0.01	0.05			due just to presence of CaCO3 in the rock (presence is indicated by ever-present foaming in digestion)
1.00	4.18			total
	5,847,675	16,010	17,593	gypsum produced, solids TPY, TPD, & TPD-up
	68.0	use it later for water bal		rock slurry % solids
0.026	130,123	356		F content of rock digested, TPY & TPD -- based on CaF2-3Ca3(PO4)2 phosphate rock
	164,457	450		H2SiF6 equivalent (presumes enough SIO2 is present in rock as is usual), TPY & TPD
0.036	179,248	491		F content of rock digested, TPY & TPD -- based on actual rock analysis
	226,545	620		H2SiF6 equivalent (presumes enough SIO2 is present in rock as is usual), TPY & TPD

Phosacid Evaporation (evap'n of water from the acid)

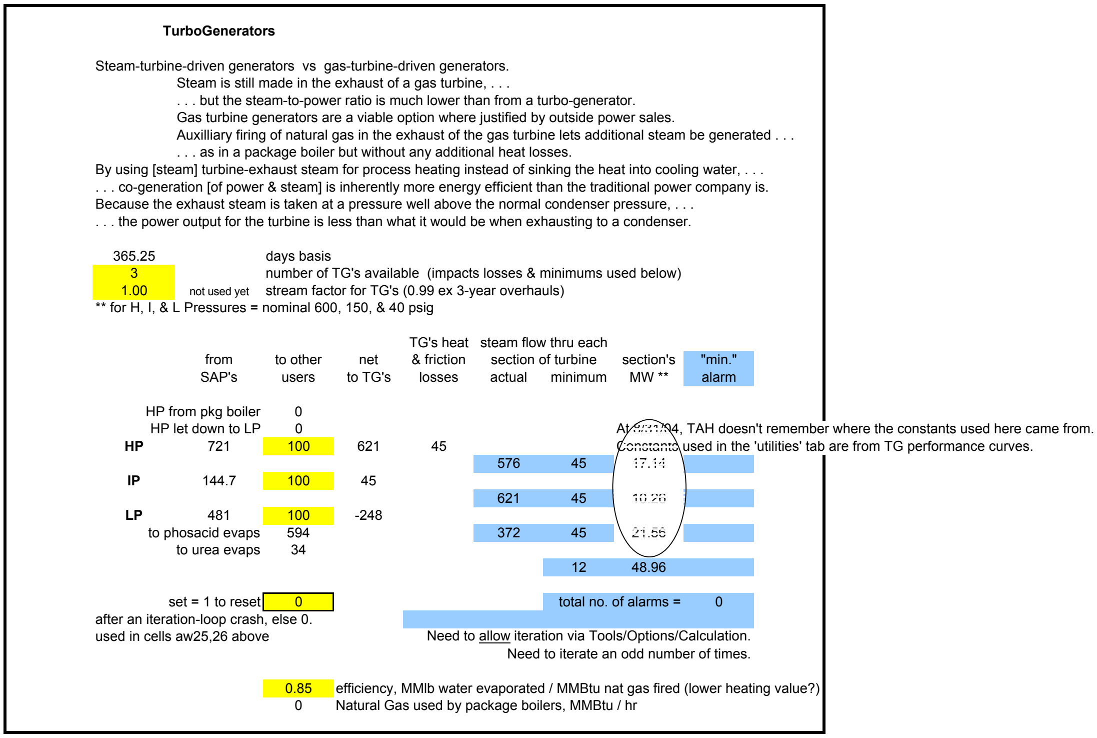
1 year	365.25	365.25	days basis for an average evaporator
1,400,000			Phosacid production, TPY P2O5
0.00			fracton of 28% phosacid bypassing the evaporators
1.00			evaporators stream factor (for individual evaps; evaps are seldom all down at the same time)
1,400,000	3,833	3,833	P2O5 run through the evaporators, TPY, TPD, & TPD-up
28.0			evaporator feed strength, % P2O5 (26-29%)
48.0			evaporator product strength, % P2O5 (45-54%)
	5,704	5,704	water evaporated, TPD & TPD-up
0.80			evaporator steam efficiency, lb water evaporated / lb steam condensed
	594	594	LP steam required, Mlb/hr & Mlb/hr-up
			(typical individual evaporator steam capacity = 30-100 Mlb/hr . . .
			. . . with lower rates at higher % P2O5.)
		3720	lb steam / T P2O5 run through evaporators
			(does not include the steam needed to bring the initial feed up to temperature.)
		48	product strength after dilution with evaporator bypass acid, % P2O5
			assume zero loss of P2O5 in evaporation.
			underflow from mid-evaporator-train clarifier does carry come P2O5 back to digestion & filtration.
			. . . & this is ~40% P2O5 unless solids are washed with "28%" P2O5 first.

Fluosilicic Acid / H2SiF6 / used for fluoridating drinking water

1 year	365.25	346.99	days basis for an average evaporator
130,123	356	375	F content of rock digested, TPY, TPD, & TPD-Fscrubber-up
164,457	450	474	H2SiF6 equivalent, TPY, TPD, & TPD-Fscrubber-up . . . which presumes enough SiO2 .
			. . . is present in the rock. FL rock has plenty. Some African rocks are short on SiO2 vs F.
24.0			Fluosilicic acid product strength, % H2SiF6 (22-28%)
1.00			evaporators stream factor (for individual evaps; evaps are seldom all down at the same time)
0.95			fluorine scrubbers stream factor vs evaporators stream factor (max 1.00)
1.00			fracton of 28% phosacid passing through the evaporators
0.60			fraction of F evaporated in evaporators (TAH wag 0.3-0.8)
0.80			fracton of evaporators with F scrubbers (weighted proportional to evap's %P2O5)
0.78	TAH wag		F scrubber efficiency that depends on product % H2SiF6, (TAH wag)
0.36			net fraction of all fluorine that is recovered (<<1.0)
58,494	160	169	H2SiF6 recovered, TPY, TPD, & TPD-up (as 100% H2SiF6)
243,725	667	702	Fluosilicic acid recovered, solution tons
83,841	230		F with other products or not recovered

Phosacid Ammoniation to make granular products

	365.25			days basis
		DAP	MAP	product
		18-46-0	11-52-0	assay, %N-P2O5-K?
	80	68.0	12.0	% split on P2O5 feed to 4 users
	1,120,000	952,000	168,000	Phosacid allocation as TPY P2O5
	495,502	452,348	43,154	NH3 feed to the 2 products, TPY NH3
	1,357	1,238	118	NH3 feed to the 2 products, TPD NH3
	2,392,642	2,069,565	323,077	ammoniation production, TPY
	6,551	5,666	885	ammoniation production, TPD
	0.90	0.78	0.12	ammoniation stream factor
4	3.60	3.11	0.49	train-years operated / calendar year **
		75.8	75.8	ammoniation production, Tons Per Train Hour-up **
		1,820	1,820	ammoniation production, Tons Per Train Day-up **
				** assume all trains have same production capacity & for either product.
				assume zero loss of P2O5 in ammoniation.
	0.999	TAH WAG		NH3 utilization in ammoniation
	1.36	loss, NH3 TPD		assume [for now] zero loss of NH3 in ammoniation.
				there are some losses to the atmosphere for which there are permit limits.
	1,358	NH3 requirements in Phosacid Ammoniation		



TurboGenerators

Steam-turbine-driven generators vs gas-turbine-driven generators.
Steam is still made in the exhaust of a gas turbine, . . .
. . . but the steam-to-power ratio is much lower than from a turbo-generator.
Gas turbine generators are a viable option where justified by outside power sales.
Auxilliary firing of natural gas in the exhaust of the gas turbine lets additional steam be generated . . .
. . . as in a package boiler but without any additional heat losses.
By using [steam] turbine-exhaust steam for process heating instead of sinking the heat into cooling water, . . .
. . . co-generation [of power & steam] is inherently more energy efficient than the traditional power company is.
Because the exhaust steam is taken at a pressure well above the normal condenser pressure, . . .
. . . the power output for the turbine is less than what it would be when exhausting to a condenser.

365.25		days basis
3		number of TG's available (impacts losses & minimums used below)
1.00	not used yet	stream factor for TG's (0.99 ex 3-year overhauls)

** for H, I, & L Pressures = nominal 600, 150, & 40 psig

	from SAP's	to other users	net to TG's	TG's heat & friction losses	steam flow thru each section of turbine actual	minimum	section's MW **	"min." alarm
HP from pkg boiler		0						
HP let down to LP		0						
HP	721	100	621	45				
					576	45	17.14	
IP	144.7	100	45					
					621	45	10.26	
LP	481	100	-248					
to phosacid evaps		594			372	45	21.56	
to urea evaps		34						
						12	48.96	

At 8/31/04, TAH doesn't remember where the constants used here came from.
Constants used in the 'utilities' tab are from TG performance curves.

set = 1 to reset 0
after an iteration-loop crash, else 0.
used in cells aw25,26 above

total no. of alarms = 0

Need to allow iteration via Tools/Options/Calculation.
Need to iterate an odd number of times.

0.85	efficiency, MMlb water evaporated / MMBtu nat gas fired (lower heating value?)
0	Natural Gas used by package boilers, MMBtu / hr

Granular Tripple Super Phosphate / GTSP

3x	Ca3(PO4)2 + 4 H3PO4 --> 3 Ca(H2PO4)2	digestion (ignoring F present in rock)
+1x	CaF2 + 2 H3PO4 --> Ca(H2PO4)2 + 2HF	(the F content)
=	CaF2-3Ca3(PO4)2 + 14H3PO4 --> 10Ca(H2PO4)2 + 2HF	digestion (including F present in rock)
	approximate compostion of phosphate rock	

3x	MW's = 310.20 + 4x98.00 = 3x234.07 = 702.2	for the
+1x	MW's = 78.08 + 2x98.00 = 234.07 + 2x20.0 = 274.1	3 reactions
=	MW's = 1008.68 + 14x98.00 = 10x234.07 + 2x20.0 = 2380.7	above
	P2O5 MW = 141.96	
	Ca(H2PO4)2 is 141.96/234.07 = 0.606 P2O5	

	1 year	365.25	357.95	days basis	
	266,000	728	743	Phosacid allocation as P2O5	
	0.999			Phosacid utilization (TAH assumes losses are pre-reaction)	
	0.98			GTSP stream factor	
	0.46			GTSP fraction P2O5 (0.45-0.46)	what is the tradition ???
rev 6/25/04	825,261	2259	2306	GTSP production, TPY, TPD, & TPD-up (0-~46-0 basis)	
				(typical plant capacity = ___? TPD)	
	75.0			rock BPL (BPL = Bone Phosphate of Lime; need 70-75 (confirm) BPL to make GTSP; . . .	
				. . . BPL = % pure Ca3(PO4)2; "pure" fluorapatite would be 92.3 BPL)	
	0.999			rock utilization (TAH assumes losses are pre-reaction)	
rev 6/25/04	332,139	909	928	rock requirements [to match phosacid], TPY, TPD, & TPD-up	
	266	0.73	0.74	Phosacid losses, TPD P2O5 & TPD-up	I'm unaware of the nature or extent
	249	0.68	0.70	rock losses, TPD P2O5 & TPD-up	of losses within the GTSP process / TAH 5/10/00
rev 6/25/04	10,697	29.3	29.9	byproduct HF, TPD & TPD-up (gets scrubbed???)	

C H E M C O M P L E X S U M M A R Y P A G E

TAH 8/13/00

HP	IP	LP	STEAM
0			from pkg boiler
0	------------>	0	HP-->LP letdown
721	144.7	481	from SAP's
100	100	100	to users other than TG's
		594	to phosacid evaps
		34	to urea evaps
621	45	-248	net available pre-TG's
621	45		to TG's
	0	248	from TG's
		3	no. TurboGenerators
		49.0	**MW generated**

	TPY	stream factor	TPD	TPD-up		365.25	days per year
	3,993,070				H2SO4 requirements in Phosacid plant		
rev 7/20/04	0				H2SO4 sales, TPY		
	3,993,070	0.940	10,932	11,630	H2SO4 total requirements to be produced		
	1,400,000	0.910	3,833	4,212	Phosacid production & distribution:		
	952,000		2,606			68	% to DAP
	168,000		460			12	% to MAP
	266,000		728			19	% to GTSP
	14,000		38			1	% to sales
						100	sum
	495,502			1,357	NH3 requirements in Phosacid Ammoniation		
	62,443			171	NH3 requirements in Urea		
	54,271			149	NH3 requirements in Nitric Acid		
	53,186			146	NH3 requirements in Ammonium Nitrate		
	59,985			164	NH3 sales		
	725,387	1.00		1,986	total NH3 requirments		
				2,277	CO2 generated in NH3 plant		
				221	CO2 to Urea plant		
				190	CO2 to MeOH plant		
				1,866	balance of CO2 to vent at NH3 plant (must be >=0)		
	75,075			210	CH4 to MeOH		
	69,444			194	CO2 to MeOH		
	200,000	0.980		559	MeOH production		
	62,443			174	NH3 to Urea		
	80,685			225	CO2 to Urea		
	110,000	0.980		307	Urea production		
					Urea to DAP		
				98	Urea to UAN solutions		
					Urea sales		
	54,271			152	NH3 to HNO3		
	196,814			550	HNO3 requirements in AmNO3		
	0			0	HNO3 sales		
	196,814	0.980		550	HNO3 production		
	196,814			550	HNO3 to AmNO3		
	53,186			146	NH3 to AmNO3		
	250,000	0.980		698	AmNO3 production		
						BPL	
	4,979,120	0.910		14,980	rock to Phosacid	64.0	
	332,139	0.980		928	rock to GTSP	75.0	
	5,847,675	0.910		17,593	gypsum produced		
	7,986	0.940		23	SO2 emissions		
	243,725	0.950		702	H2SiF6 produced		
	83,841			230	F with other products or not recovered		
					%AmNO3 to UAN solutions	30.0	tah wag wag
	9,211		25		AmNO3 (100% basis) to UAN solutions		
	35,966		98		Urea to UAN solutions		
	20,000		55		UAN produced, tons of N		

AmNO3 & Urea demands by UAN solutions
are not accounted for in those production units YET / TAH 5/12/00

wet-process phosphoric acid (vs furnace acid for high-purity uses)
H_3PO_4
grinding, digestion, & filtration

IMC-Agrico, Uncle Sam & Faustina Plants
PCS Nitrogen, Geismar

phosphate rock grinding

- Grinding is needed for efficient & complete digestion -- except when using some already-fine African rock sources.
- Coarse material can get coated with byproduct gypsum before it has a chance to digest.
- Fine material may digest too fast, upsetting temperature & concentration profiles that impact the critical growth of byproduct gypsum.
- At the end of cheap natural gas contracts in the late 1970's, grinding was converted from dry-basis to wet-basis to eliminate the cost of rock drying.

digestion / "attack":

- 98% H_2SO_4 + H_2O --> 2% H_2SO_4 Btu heat of dilution
- $Ca_3(PO_4)_2(s) + 3\ H_2SO_4 + 6\ H_2O \rightarrow 3\ CaSO_4\text{-}2H_2O(s) + 2\ H_3PO_4$ Btu
- Phosphoric acid strength is usually reported as % P_2O_5, the anhydrous equivalent that never exists in a wet-process phosacid plant.
- Phosphate rock is actually a ~fluo-apatite that contains fluorine which is liberated as F^- (=HF) during digestion.
  - Since Fluorine fumes are irritating, they are drawn from the attack tank & filter & are scrubbed with water.
- The digester is normally a multi-compartment "attack" tank with rock & H_2SO_4 feeds and the draw-off for the filter all in different compartments.
  - Circulation through the several compartments minimizes the Ca & SO_4 gradients as needed to complete digestion . . .
    - and to form big/filterable gypsum crystals. Filtration is typically the rate-limiting step.
  - Circulation time is ~10 minutes vs average residence time of ~3 hours.
  - Circulation also goes through flash cooling to remove the heats of H_2SO_4's dilution and reaction with Ca^+
- Scale control dictates much of plant design for digestion/attack & filtration, etc.
- The combination of digestion temperature and H_2SO_4 concentration must be limited to prevent formation . . .
  - of $CaSO_4\text{-}o.5H_2O$ that hydrates, cementing as a solid mass of plaster of Paris.
  - Reaction temperature is normally limited to 195oF for this reason.
  - Heat-removal limitations normally keep temperatures near an upper limitation.
  - At some low temperature I presume digestion and crystallization rates become limiting.

& filtration (of gypsum byproduct):

- A slurry of gypsum-in-phosacid is fed to a filter where the gypsum gets 1-2 stages of counter-current washes with gypsum pond water.
- The strong-wash water goes to the attack tank to control filtrate SpGr (which is a crude indicator of viscosity) as one control of filterability.
- The product filtrate goes to clarification, [to solvent extraction,] & to evaporation.
- Washed gypsum is slurried with pond water for pumping to a gypsum stack.
- In the stack, the gypsum settles and clear pond water is decanted for reuse:
  - Gypsum pond water is used for washing gypsum filter cake and for slurrying the washed cake.
  - Another new-in-the'90's use for pond water is as makeup water in wet rock grinding.
    - pH adjustment & mill modifications are usually needed to minimize corrosion in the mill.
    - The purpose is to:
      - Recovery more of the P_2O_5 in the pond water [when pond water supply is adequate].
      - Minimize import of fresh water into a contaminated-water system where, as in Louisiana, rain already makes the volume grow.
        - To control water volume, any water discharged must be treated to cut the P & F contents.
        - Permits have daily and monthly limits for tons of P & tons of F.
        - Typically, P&F are precipitated with lime and the water is clarified for discharge.
        - Attempts have been made to demonstrate use of reverse osmosis, but the challenges & capital requirements are great.
        - Solids from the clarifier underflow are as concentrated (????) a source of P_2O_5 as phosphate rock is and should be recycled somehow to the process.
- Pond water (with gypsum settled out) is used for washing so some of the P_2O_5 values in the pond water can be recovered.
  - Any fines in the pond water can severly reduce wash rates. Fines can come from:
    - Short circuiting in the gypsum-settling pond.
    - Super-saturation with fluosilicates. This can be troublesome in the year's coldest periods when the gypsum pond hasn't been recently diluted by rain.
    - Where wash water is heated in a barometric condenser, fines can also be introduced by acid carryover.
  - Fresh water is used for washing only when:
    - Pond water fines hurt wash rates too badly, or
    - Pond water supply is low due to low rainfall. Then to maximize P_2O_5 recovery, the fresh water should be added to the pond vs to the filter.
- By heating the wash water, the water's viscosity is reduced to increase wash & filtration rates.
  - Heating is frequently done by in the barometric condenser of the attack tank's flash cooler.
  - Any condensate from the cooler's vacuum-producing steam jets is also added to the wash water.
  - Heating has been done in an evaporator's fluorine scrubber.

Can make liquid fertilizers from "70%" P_2O_5 phosacid IF that acid is made from <u>high</u> purity phosphate rock & acid solids are removed [or stabilized?/TAH].
PCS Phosphates makes LoMag, a 0-70-0 superphosphoric acid.

Major revisions made to this tab on 6/30/04 by TAH.

Phosphoric Acid Producton

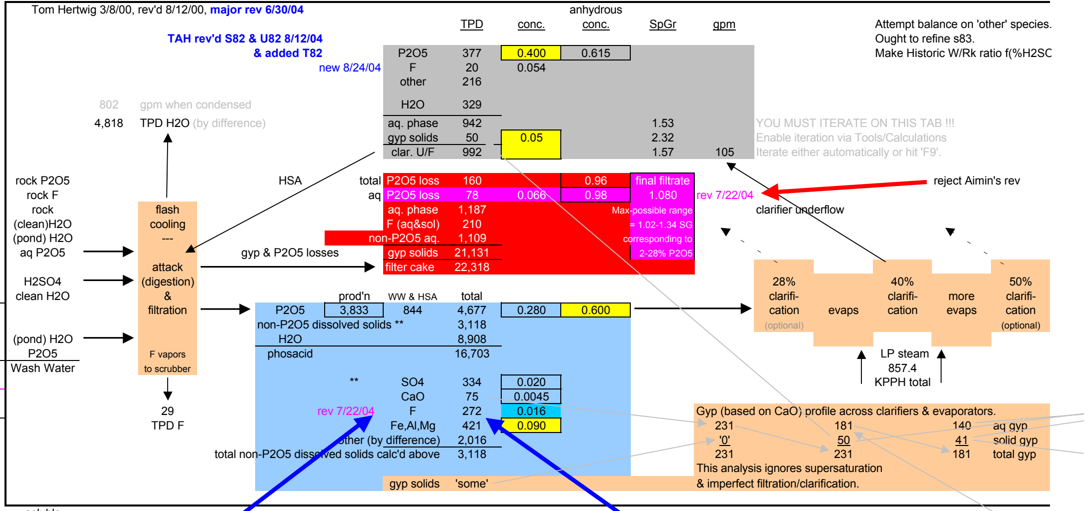
Tom Hertwig 3/8/00, rev'd 8/12/00, **major rev 6/30/04**

TAH rev'd S82 & U82 8/12/04
& added T82

Attempt balance on 'other' species.
Ought to refine s83.
Make Historic W/Rk ratio f(%H2SC

	conc.	gpm	TPH	TPD	
[dry basis] frac. pure Ca3(PO4)2 = BPL/100 =	0.64		166	3,993	rock P2O5
new 8/24/04 TAH --> [dry basis] rock F =	0.036		20	491	rock F
rock slurry solids fraction =	0.68		568	13,632	rock
water content of damp rock fed to ball mill =	0.10	252	63	1,515	(clean)H2O
		800	200	4,802	(pond) H2O
			4	98	aq P2O5
H2SO4 conc. =	0.985		456	10,932	H2SO4
		28	7	166	clean H2O
		1,008	462	11,099	
for A/T Filt SpGr control:					
water feeds (ex-HSA) gpm / TPH Rock =	7.20	3,010	753	18,074	(pond) H2O
frac P2O5 =	0.02		15	369	P2O5
			768	18,443	Wash Water

Gyp repulp water is not included in the flows here.		
	WS P2O5 gain	467
	total P2O5 loss	1347
	net gain	-880



	TPD	conc.	anhydrous conc.	SpGr	gpm
P2O5	377	0.400	0.615		
F	20	0.054			
other	216				
H2O	329				
aq. phase	942			1.53	
gyp solids	50	0.05		2.32	
clar. U/F	992			1.57	105

YOU MUST ITERATE ON THIS TAB !!!
Enable iteration via Tools/Calculations
Iterate either automatically or hit 'F9'.

total	P2O5 loss	160		0.96	final filtrate
aq	P2O5 loss	78	0.066	0.98	1.080
	aq. phase	1,187			Max-possible range
	F (aq&sol)	210			= 1.02-1.34 SG
	non-P2O5 aq.	1,109			corresponding to
	gyp solids	21,131			2-28% P2O5
	filter cake	22,318			

	prod'n	WW & HSA	total		
P2O5	3,833	844	4,677	0.280	0.600
non-P2O5 dissolved solids **			3,118		
H2O			8,908		
phosacid			16,703		

**	SO4	334	0.020
	CaO	75	0.0045
rev 7/22/04	F	272	0.016
	Fe,Al,Mg	421	0.090
	other (by difference)	2,016	
total non-P2O5 dissolved solids calc'd above		3,118	
	gyp solids	'some'	

Gyp (based on CaO) profile across clarifiers & evaporators.

231	181	140	aq gyp
'0'	50	41	solid gyp
231	231	181	total gyp

This analysis ignores supersaturation & imperfect filtration/clarification.

accept Aimin's rev

	insoluble	soluble	insoluble	soluble		
3x	**Ca3(PO4)2 + 3 H2SO4 + 6 H2O --> 3 CaSO4-2H2O + 2 H3PO4**					reaction when F-content is ignored
	~65BPL (=65% purity)		3 x 172	1 x 142	3.63	

+1x CaF2 + H2SO4 + 2 H2O --> CaSO4-2H2O + 2 HF

= **CaF2-3Ca3(PO4)2 + 10 H2SO4 + 20 H2O --> 10 CaSO4-2H2O + 2 H3PO4 + 2 HF** net reaction including F from fluor- in fluorapatite (rock)
fluorapatite

produce 1 ton of P2O5 per (1*310MW/~~(2*98MW)~~ * ~~(2*98MW)~~/(1*142M) /0.65purity /0.95recovery =) 3.54 ton of rock.

per 1 ton of rock, we use > (((3*98MW) + 0.02*(2*98)) / (1*310) *0.65purity =) 0.62 ton of [100%] H2SO4
The CaCO3 present bumps the actual ratio up to ~ 0.77 T H2SO4 / T rock

Typ. F balance in TPH for 1000 TPD P2O5 DiHydrate plant
p106 of FCI Fertilizer Technical Data Book, 1994

Rock feed	4.96	TPD F	Does NOT
vapors	0.29		account for F
gypsum	1.92		recycle w/ HSA
30% P2O5 product	2.75		TAH 8/24/04
net check =	0.00		

Rock feed	491	TPD F	Values
HSA	20		from
vapors	29		the
gypsum	210		plant
30% P2O5 product	272		modeled
net check =	0	OK	above

6/30/04, these 3 values	0.802	SA/rk ratio
are now imported from	0.91	PAP stream
the 'complex II' tab	0.94	SAP stream
	0.776	net

lb LP steam needed to evaporate 1T of phosacid from 28% to 50% P2O5.
4400 lb/T

	TPY P2O5 (90% uptime)	**TPD-up P2O5**		TPH-up rock	**TPD-up H2SO4** req'd if same 90% up		LP steam needed by evaporators	TAH WAG capital $ MM
US	433,000	1320	existing	194.7	3628		242,000	0
US	433,000	1320	existing	194.7	3628		242,000	0
US	197,000	600	expansion	88.5	1649		110,000	20
US	197,000	600	expansion	88.5	1649		110,000	20
Fau	537,000	1635	existing	241.2	4494		299,750	0
Fau	197,000	600	expansion	88.5	1649		110,000	12
Fau	197,000	600	expansion	88.5	1649		110,000	17
US	866,000			389	7,256		484,000	
Fau	537,000			241	4,494		299,750	
existing-plants totals	1,404,000	4,275		631	11,749	vs 11,600 produced on "H2SO4" tab	783,750	
total w/ expansion #1	1,601,000	4,875		719	13,398	= up 1,627	893,750	
total w/ expansion #2	1,798,000	5,475		808	15,047	= up another 1,627	1,003,750	

expansion #1 is to total 600 TPD P2O5
expansion #1+2 is to total 1200 TPD P2O5

Molecular Weights	
310	Ca3(PO4)2
98	H2SO4
18	H2O
172	CaSO4-2H
98	H3PO4
0	net
142	P2O5
56	CaO
136	CaSO4

Operating Costs:
+ $2/T P2O5 barged between plant sites
+ $25/T rock delivered to plant
+ $0.2/T gyp pond water pumped to plant

4).

Phosphoric Acid Evaporation

accept Aimin's rev.

	TPD	conc.	anhydrous conc.
F	118		
H2O	6,445.8		
rev 7/22/04 P2O5	4,300	0.480	0.630
non-P2O5 dissolved solids ***	2,525		
H2O	2,133		
phosacid	8,958		
SO4 (aq)	283	0.032	
46 CaO (aq)	34	0.0038	
??? F	154	0.036	
Fe,Al,Mg	387	0.090	
other (by difference)	1,667		
total non-P2O5 dissolved solids calc'd above	2,525		
gyp solids	41		

rev 7/22/04

Fluorine scrubbers

	TPD	conc.
F	11.5	
H2O	6,445.8	
H2SiF6	97.5	0.24
H2O	308.7	
HFS acid	406.1	
(or approx.	55	gpm)

H2O

F recovery = f(%H2SiF6 & evaporator staging) = 0.903 roughly.

old TAH wag = 95 - 2x%H2SiF6

MW	
19	F
28	Si
104	SiF4
144	H2SiF6

0.480 0.5112 US actual conc

0.036 0.030 textbook ratio

0.0153 textbook conc

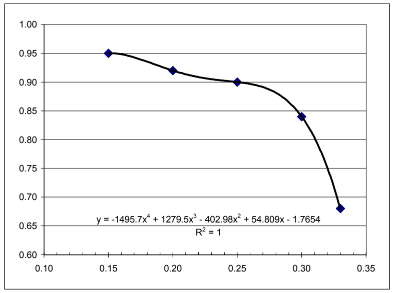
close !

0.0169 US actual conc

Data from table on p105 of FCI Fertilizer Technical Data Book, 1994

	% H2SiF6	% recovery
65	0.15	0.95
55	0.20	0.92
45	0.25	0.90
35	0.30	0.84
29	0.33	0.68

TAH's old wag recovery.



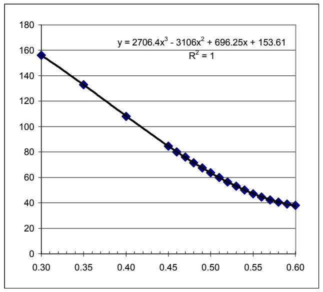
FCI Fertilizer Tech Data Book p79 gyp solubility at 80oC	x 56/172 = % CaO	typ % CaO	typ % SO4	calc'd Ksp
1.35%CaSO4 at 28% P2O5	0.556	?	2.4	1.33
1.06%CaSO4 at 40% P2O5	0.436			
0.82%CaSO4 at 48% P2O6	0.338	0.29	4.09	**1.19**
FCI Fertilizer Tech Data Book p80		~~%CaSO4~~???		
for crude Phosacid		%CaO	%SO4	
25% P2O5		0.46	1.57	**0.72**
32% P2O5		0.56	1.57	**0.88**
25% P2O5	**IFFF really**	0.189	1.57	0.30
32% P2O5	**'CaSO4' in graph**	0.231	1.57	0.36
FCI Fertilizer Tech Data Book p81				
30% P2O5	sat'n	0.41	2	**0.82**
	super-sat'n	0.65	2	**1.30**

2

2O

NEW 8/24/04 TAH

% P2O5	**lb F / T P2O5**	TAH's model	model error
0.30	156	156.0	0.0
0.35	133	132.8	-0.2
0.40	108	108.4	0.4
0.45	84.5	84.6	0.1
0.46	80.0	80.1	0.1
0.47	76.0	75.7	-0.3
0.48	71.5	71.5	0.0
0.49	67.5	67.4	-0.1
0.50	63.7	63.5	-0.2
0.51	59.9	59.8	-0.1
0.52	56.4	56.3	-0.1
0.53	53.0	53.1	0.1
0.54	50.0	50.0	0.0
0.55	47.0	47.3	0.3
0.56	44.6	44.8	0.2
0.57	42.4	42.5	0.1
0.58	40.6	40.6	0.0
0.59	39.0	39.0	0.0
0.60	38.0	37.8	-0.2



Data read from graph on p107 of FCI Fertilizer Technical Data Book, 1994

methanol / methyl alcohol
CH3 OH or MeOH/TAH

BCP, Geismar	*used to make Acetic Acid & Formaldehyde on-site & MTBE off-site*
Ashland, Plaquemine	*no downstream products made on-site; CO2 from IMC-Agrico Faustina; plant now down*
Cytec, Westwego (NH3 plant converted to MeOH)	
Georgia Gulf, Plaquemine	

Synthesis gas preparation:

- CH4 + H2O -(catalyst)-> CO + 3H2 **steam reforming**
  - Reaction is favored by high temp (very endothermic) & low press (no. of moles doubles)
  - Reaction produces 1:3 CO / H2 vs the 1:2 needed for MeOH synthesis, so another source of CO or CO2 must be added. Options:
  - **o** Import CO. (Is this done? BCP & Ashland imported CO2 instead)
  - **o** Import CO2 & "shift" it back to CO by consuming some of the H2 produced from CH4.
    - CO2 + H2 -(catalyst)-> CO + H2O **water-gas shift** reaction (run in "reverse" / TAH explanation. ok?)
    - This is the reverse of the "water-gas shift" reaction used in the NH3 process. (TAH explanation. ok?)
    - CO2 is "shifted" back to CO by comsuming some of the H2 produced from CH4.
    - The CO2-to-CH4 molar feeds ratio needs to be 1:3 to get 1:2 CO / H2 for MeOH synthesis . . .
      - . . . though any incomplete conversion of CO2 would call for a slightly higher feeds ratio.
    - **3x** CH4 + H2O -(catalyst)-> CO + 3H2
    - **+1x** CO2 + H2 -(catalyst)-> CO + H2O
    - = 3 CH4 + 2 H2O + CO2 ---> 4 CO + 8 H2 net reaction
    - How complete is the conversion of CO2 to CO ? / TAH
      - Unconverted CO2 will waste CO2 feed & carry MeOH, etc. with it when it has to be purged from the synthesis loop. (TAH explanation. ok?)
        - Purge stream goes to the reformer with the fuel.
      - CO2 conversion is hurt by the steam that is essential to H2 generation, so . . .
      - . . . careful control of steam-to-carbon ratio must be needed to minimize CO2 fed to synthesis. (TAH explanation. ok??)
      - . . . The stoichiometric molar ratio is 2:3 as calculated above.
      - The "forward" shift reaction, as used in the NH3 process, is favored by low temp (mildly exothermic) & is unaffected by press . . .
      - . . . so maybe higher temperatures will favor the "reverse" shift reaction needed in the MeOH process. (TAH explanation. ok?)
  - **o** CH4 + o.5O2 --> CO + 2H2O partial oxidation
    - This would supply CO ok, but would introduce much N2 as inerts to this process.
    - This is analogous to the secondary reformer in an NH3 plant.
    - Is this ever done ??? / TAH

- (CO + H2O -(catalyst usually)-> CO2 + H2 water-gas shift reaction; MUST BE RUN IN REVERSE IN MeOH PLANT !!!!
  - Excess steam is used to force the reaction to completion (via equilibrium constant).
  - In the NH3 plant, this reaction occurs with reforming in the primary reformer that operates at 760-980oC.
  - Product composition depends on process conditions:
    - Temp, press, & excess steam determine equilibrium.
    - Velocity through the catalyst bed determines approach to equilibrium.
    - Typical product is 75% H2, 8% CO, 15% CO2, 2% balance = N2 + CH4.

- This partial oxidation is needed to cut the H2:CO ratio from 3.0 for steam reforming to the 2.0 needed to make MeOH. / TAH
- The inerts purge will keep the goal ratio from being an exact integer / TAH.
- ALTERNATELY, the extra CO might (???) be supplied by an ammonia plant . . . but they normally have CO2 as a byproduct vs SO …

p763 Economical preparation of syngas is vitally important for its cost = 75% of final cost of MeOH.
Both HP & LP partial oxidation proceses are used.

Synthesis gas p 95-97 Both CO & H2 come from synthesis gas (steam reforming / TAH).
[MeOH] synthesis pressure = ~3 MPa (vs ~8 MPa in earlier years).
- Can now use centrifugal compressors. Must cool to remove heat of compression to control converter temp.

p764, p93 Because the catalyst is sensitive to sulfur, sulfur must be removed from the syngas (vs from nat gas feed to syngas prep?).
- Several sulfur-removal processes are available.
- Traditional process uses an aqueous solution of MEA or MDEA to scrub the gas.
  - p93 Alternate solvents vary in selectivity for absorption of H2S vs CO2.
- p94 Membrane separation processes are also used. These typically have lower energy & capital costs.
- p92 Raw natural gas can contain up to 35g/m3 of H2S

MeOH synthesis in catalytic converter:

Shreve p763 CO + 2H2 --> CH3OH DH = -103 MJ (confirm since p763 listed only 1H2)
Use copper-based catalyst (vs zinc-chromium in earlier HP process).
Developing liquid-entrained micron-sized catalysts that can convert as much as 25% per pass.
If synthesis gas contacts hot iron, competing reactions are catalyzed and volatile iron carbonyl forms, fouling the copper catalyst.

p764 Equilibrium constant, Kp = 1.7E-2(200oC), 1.3E-4(300oC), 1.1E-5(400oC)
- So converter operating temp is another tradeoff between kinetics & equilibrium / TAH.
- The converter in the Lurgi LP plant sketched runs 5-8MPa & 250-260oC.

Conversion to liquid MeOH in 1 pass at 300oC = 8.0%(500MPa), 24.2(1000), 48.7(2000), 62.3(3000)
- Implies only trace conversion at typical 5-8MPa !?! / TAH

2 types of reactors are used:
- Bed-in-place reactor has heat recovery only on the exit gas and can make enough 4.5MPa steam to drive the compressor.
- A multi-tray reactor introduces cool feed gas above each bed for more-isothermal operation. Similar to Kellogg's ammonia process.
  - Conversion-per-pass is higher (/TAH), but heat recovery is more difficult.

Exit the single-stage converter:

- MeOH is condensed by both heat exchange and pressure reduction.
- Condensed MeOH is collected and purified. High-boiling & low-boiling impurities are removed in 2 columns.
- Unreacted materials are recycled after an inerts purge. TAH assumes purge gas is used for fuel in syngas prep as in the ammonia process.

sulfur production & storage

Frasch sulfur

160oC water is injected via double-pipe annulus into porous sulfur-bearing rock formation
& melted sulfur returns (along with some hot water) in center pipe.
Shreve p 321-3 It takes ~months to melt sulfur in a totally-new area. New offset wells must be drilled periodically to boost production rates.
& TAH Sulfur-melting water is heated in natural-gas-fired package boilers. This water is "fresh" on-shore & "sea/salt" off-shore.
Corrosion is a major problem, especially with sea water.
Power generators for these typically-remote locations are driven by steam turbines that are fed by [clean-water] package boilers.

Claus sulfur

$H_2S(g) + 1.5\ O_2 \rightarrow SO_2(g) + H_2O(g)$ DH = -518.8 k require 98% conversion in 1984 (99.5% in Alberta provin
Shreve p 323-4 $SO_2(g) + 2H_2S(g) \xrightarrow{Fe_2O_3} 3S(l) + H_2O(g)$ DH = -142.8 k presume balance is SO_2 air emissions
H_2S is recovered from sour natural gas & oil refining by absorbing it & re-releasing it in fairly pure form.

sulfur storage

Trace hydrocarbon content in sulfur + S --> H_2S that must be air-stripped to prevent accumulation of lethal or explosive levels of H
TAH The total pounds of H_2S are few and no recovery attempt is made.

sulfuric acid process
H2SO4

IMC-Agrico, Uncle Sam & Faustina Plants (for phosacid)
PCS Nitrogen, Geismar (for phosacid)
DuPont, Burnside (regeneration plant tied to refinery)
Rhodia, BR (regeneration plant tied to refinery)
Cytec, Westwego (regeneration plant tied to MMA plastics plant)

Reactions:

Shreve p329-40 S + O2 --> SO2 DH = -298.3 kJ, 26oC
p331 SO2 + 0.5 O2 <-(V2O5)--> SO3 DH = -98.3 kJ, 26oC
p331 H2O + SO3 --> H2SO4 DH = -130.4 kJ, 26oC
p335 n2(SO3) = n2(SO2) x n(O2) x Kp x P / N where n = no. moles; P = total Press.; N = total moles; &
p333 equilibrium constant Kp = f(temp) = 397(400oC), 48.1(500), 9.53(600), 2.63(700), o.915(800), o.384(900), o.1845(1000), o.o980(1100)
p331 Rearranged, Kp = p(SO3) / (p(SO2) x p(O2)o.5)
p335 So: O2 & P help. Temp & SO3 hurt -- need to cool & inter-stage-absorb-SO3 to get high conversion.
SO2 oxidation is catalyzed. Reaction rate increases with temperature as is traditional, ...
but reaction slows on the low side below the catalyst "ignition temperature" of ~720oF and on the high side as SO2-SO3 equilibrium is approached.

TAH **Air-Drying & SO3-Absorption Towers:**

- Commercial processes add SO3 to 98.5% H2SO4 & water to the resulting 99% H2SO4.
  - SO3 absorption is most complete at 98.5% and there it is essentially complete.
    - Poorer-than-normal absorption can make the stack gas visible as a white plume of H2SO4 mist.
    - Stack gas opacity is a concern because there are limits in the operating permit and opacity may indicate a steam-system leak.
      - High-performance demisters will capture some of the mist and hide the steam-system problems for awhile.
    - Other potential causes for opacity include low absorber acid temperature & high absorber gas-inlet temperature.
- Product H2SO4 can be taken off as dilute as 93% with little extra risk of corrosion. Corrosion accelerates rapidly below 92%.
  - Lower strengths (93 vs 98) are valuable only to reduce heat of dilution in subsequent use.
- Air drying is needed to reduce risk of acid condensing in the gas-side of the process.
  - Air is dried with H2SO4 -- cooler acid is much better & 98% is slightly better than 93%.
  - Dew point is typically ~~-40o and can be estimated from H2SO4 partial-pressures tables.

Waste heat recovery:

- Waste heat is recovered from gas streams above 300oF as 600 or 900 psig superheated steam.
  - Heat recovery from gas upstream of acid is limited by the gas dew point of 280-300oF.
    - Dew point depends on the hydrocarbon content of the sulfur feed & drops ~20oF after being dried in the 1st SO3-absorption tower.
  - The 300 psi gap in steam-system designs is because turbine metallurgy must be more exotic above 750oF, a reasonable superheat for 600 psig.
- Increasingly, heat is recovered also at an intermediate pressure to recover lower-grade heat.
  - Heat of SO3 absorption can be recovered with Monsanto Enviro-Chem's HRS (Heat Recovery System).
    - This heat is recovered as 150(confirm) psig steam.
- Process heat recovery is ~~70% without HRS & ~~80% with HRS. Most losses go to acid-cooling water.

Production rates:

- H2SO4-TPD-to-steam-MPPH production ratio runs 9.2 +/- 0.5 (w/o HRS).
  - The ratio changes with ambient temp., wind, rain, & fuel:air ratio (that is adjusted to keep stack SO2 within permit limits).
- H2SO4 producton capacity is normally limited by blower capacity and increases at night and in winter when inlet air is cooler/denser.

Regeneration process:

DuPont, Burnside
Cytec, Westwego
Rhodia, BR

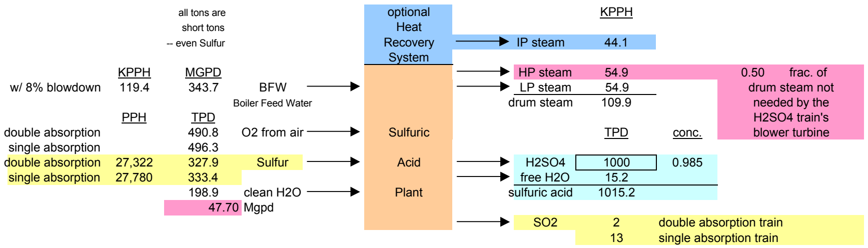
- Spent H2SO4 contains organics from refinery.
- Spent H2SO4 is decomposed in nat-gas-fired burner to SO2, H2O, CO2, etc.
- Gunk is periodically removed from waste-heat-recovery boiler by manual rodding. This is done on-line since boiler is under slight vacuum.
- From the gas, condensibles are removed and particulates filtered out before feeding SO2, N2, O2 to sulfur furnace of a standard sulfuric plant.

Oleum option:

- SO3 absorption tower run in parallel to normal-sulfuric plant's primary(?) absorption tower.
- Just control at a different strength H2SO4.

Sulfuric Acid Producton

Tom Hertwig 2/24/00



32 48 18 98

S + 1.5 O2 + H2O --> H2SO4

S + O2 --> SO2; SO2 + 0.5 O2 --> SO3; SO3 + H2O --> H2SO4

produce 1 ton of 100%-basis H2SO4 per (32MW/98MW /~0.999purity /0.9975recovery =) 0.3277 ton of sulfur.

produce 1 ton of 100%-basis H2SO4 per (32MW/98MW /~0.999purity =) 0.3268 ton of sulfur.

H2SO4 production is typically 9.1 TPD * drum steam Klb/hr. (does not include HRS steam)

Assume for now that the optional Heat Recovery System generates 150Mlb/hr of IP steam from a 3400TPD plant.

IP = "Intermediate Pressure" steam = ~150psig.

SO2 emissions limit is 4 lb SO2 / T H2SO4 produced . . . .

. . . . except for the one 1800-TPD single-absorption train that has an effective limit of ~26. Lb SO2 / T H2SO4 produced

Require no increase in 2-site SO2 emissions if single-absorption plant is operated.

Allow an increase if single-absorption plant is NOT operated.

Plant rate can be turned down no lower than 50% of nominal capacity.

Minimum nominal capacity = 1800 TPD. The "900" minimum listed below is 1800 at 50% rate.

MW	
32	S
98	H2SO4
32	O2
64	SO2
80	SO3

Sulfuric Acid Plants

given:	4,275	TPD-up 30% P2O5 production
	0.91	PAP stream factor
	0.94	SAP stream factor
	4,139	TPD-up H2SO4 requirements
	4.0	stack SO2 emissions, lb SO2 / T H2SO4 produced (max 4.0)
	8.28	stack SO2 emissions, TPD-up
	0.001	sulfur impurities, decimal fraction; ash & hydrocarbons
	1,357	sulfur requirement, TPD-up (short tons & including impurities)
	0.08	boiler blowdown as fraction of BFW feed (typ = 0.05-0.10)
	9.1	TPD H2SO4 / Mlb/hr of HP drum steam (typ = 8.5-9.7, not including IP steam)
	0.50	fraction of HP drum steam used by blower turbine (typ = 0.35-0.60)
	454.8	drum steam, Mlb/hr
	227.4	steam to blower turbine, Mlb/hr
	494.3	Boiler Feed Water, Mlb/hr
	988	BFW, gpm
	39.5	blowdown, Mlb/hr
	0.3	fraction of SAP capacity with Heat Recovery System producing IP steam
	150	Mlb/hr IP steam from a 3400 TPD SAP with HRS
	54.8	Mlb/hr IP steam
	0.985	sulfuric product concentration (0.93-0.99; 0.985 minimizes stack opacity)
	823.2	dilution water required, TPD-up
	137.1	dilution water required, gpm

site	full rate **TPD H2SO4**	Heat Recovery System		capital $ MM	any-rate operating Δ$ MM/yr	full-rate SO2 TPD	full-rate HP steam Kpph	full-rate LP Steam Kpph	full-rate IP steam Kpph
US	3400	--	existing	0	0	6.8	186.8	186.8	0
US	(3400)	HRS	new	6	0	0	0	0	150
US	1800	--	existing	0	0	3.6	98.9	98.9	0
US	1800SA	--	existing	0	0	23.4	98.9	98.9	0
US	1800DA	--	conversion	16	0	3.6	98.9	98.9	0
US	2600DA	--	conv&upgr	22	0	5.2	142.9	142.9	0
US	X=900-3400	--	new	13.14+0.0066X	0	X*4/2000	X*0.5/9.1	X*0.5/9.1	150*X/3400
US	X=900-3400	HRS	new	15.51+0.0080X	0	X*4/2000	X*0.5/9.1	X*0.5/9.1	150*X/3400
Fau	2300	--	existing	0	0	4.6	126.4	126.4	0
Fau	2300	--	existing	0	0	4.6	126.4	126.4	0
Fau	X=900-3400	--	new	13.14+0.0066X	0.5	X*4/2000	X*0.5/9.1	X*0.5/9.1	150*X/3400
Fau	X=900-3400	HRS	new	15.51+0.0080X	0.5	X*4/2000	X*0.5/9.1	X*0.5/9.1	150*X/3400
US	7,000						384.6	384.6	
Fau	4,600						252.7	252.7	
existing-plants totals	11,600	--	existing	0	0	43	637.4	637.4	0
needed now	11,749								
needed w/ expansion #1	13,398	= up 1,627							
needed w/ expansions #1&2	15,047	= up another 1,627							

	LP steam				HP steam															
						used for LP steam												MW of power gen.			
	total needed	produced by SAP's	produced via other turbines	bal. needed from TG's	produced by SAP's	via other turbines	via TG's	used elsewhere	bal. avail. for power	no. of TG's	MW of power generated (before adding IP steam)	ΔMW vs now	TPD H2SO4 w/ HRS min	max	IP steam KPPH min	max	no. of new TG's	from IP steam min	max	from IP+HP min	max
US	484.0	384.6	40	59.4	384.6	40	33.0	60	251.6	2	23.1		0	0							
Fau	299.8	252.7	47.0	0	252.7	47.0	0.0	205.7	0	0	---		0	0							
available now:	783.8	637.4	87.0	59.4	637.4	87.0	33.0	265.7	251.6	2	23.1		0	0							
needed now:	783.8	645.6	87.0	51.2	645.6	87.0	28.4	265.7	264.4	2	24.4		0	0							
needed w/ expansion #1	893.8	736.2	87.0	70.6	736.2	87.0	39.2	265.7	344.2	3	31.2	6.8	1627	5027	71.8	221.8	1	3.8	14.9	10.5	21.7
needed w/ expansions #1&2	1003.8	826.8	87.0	90.0	826.8	87.0	50.0	265.7	424.0	4	37.9	13.5	3254	6654	143.6	293.6	2	7.6	18.7	21.1	32.2

"min" case just includes HRS on the new sulfuric plant.
"max" case also includes HRS on US's existing 3400 TPD plant.
The "2" TG's could be just 1 if analysis recommends the "2" be at the same plant site.

Operating Costs:
+ $100/T Sulfur as a raw material. (=$100x32/98 / T H2SO4)
+ $o.3/1000gal of clean water as raw material -->$o.o1/T SA
+ $1/1000gal of Boiler Feed Water makeup -->$1.4/T SA
+ $2/T H2SO4 for operating cost
+ $200K/yr for extra operator to run new SAP at Fau
+ $1/T H2SO4 barged between plant sites

1000 gal = 1000 x 8.34 / 2000 = 4 tons
o.10-o.25/Kgal process water Perry p 26-29 (1960)

Capital Costs:
$5MM for new tanks if barging > 500 TPD H2SO4

TPD	capital $MM (1997)	$vsTPD model	model error	model % error
3400	33.40	33.58	0.18	0.54
3300	32.81	32.92	0.11	0.34
3200	32.21	32.26	0.05	0.16
3100	31.60	31.6	0.00	0.00
3000	30.98	30.94	-0.04	-0.14
2900	30.36	30.28	-0.08	-0.26
2800	29.73	29.62	-0.11	-0.36
2700	29.09	28.96	-0.13	-0.43
2600	28.43	28.3	-0.13	-0.47
2500	27.77	27.64	-0.13	-0.48
2400	27.10	26.98	-0.12	-0.45
2300	26.42	26.32	-0.10	-0.37
2200	25.72	25.66	-0.06	-0.24
2100	25.01	25	-0.01	-0.06
2000	24.29	24.34	0.05	0.19
1900	23.56	23.68	0.12	0.52
1800	22.80	23.02	0.22	0.94
1000	16.03	17.74	1.71	10.69

TAH
2/29/00

	0.006602	11.14579759
	5.85E-05	0.154744165
	0.998824	0.118139558
F	12741.44	15
	177.8316	0.209354328

→

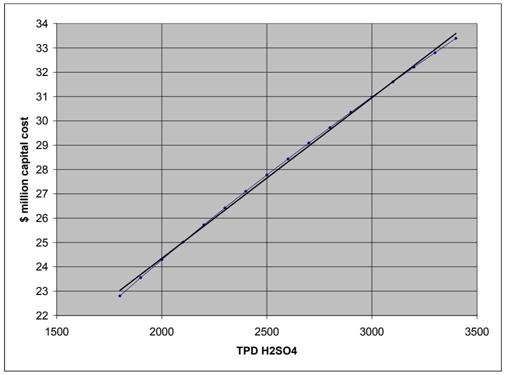
40/33x w/ HRS

0.0080024	13.5100577

$MM = 11.14 + TPD * 0.0066 $MM = 13.51 + TPD * 0.0080

$MM = 13.14 + TPD * 0.0066 $MM = 15.51 + TPD * 0.0080

& add $2MM for cooling tower
or river water pumps
for a new SAP of any size.



utilities

power & steam

see also LA Petrochemical Industry CoGen analysis, 7/83/TAH copy

power generation via steam turbine

Energy Handbook p407 Typical heat? rate is 8,500-9,600 lb steam per MWH generated.
Steam usage depends on turbine efficiency (no. of wheels & vintage), & feed-steam superheat. (& pressure for the same degrees of superheat)
p407 8,800 btu / KWH was typical for coal-fired power plants in 1979

power generation via gas turbine

Gas turbine's typical heat rate is < than for a steam turbine since the gas turbine's hottest temp >> that of steam.
Heat rate depends on combustion temperature (impacts maintenance & NOx) & extent of waste heat recovery:
Gas turbines are of 2 different classes:
"Aircraft derivatives" that run hot all the time. In jets, these turbines run hottest only during takeoff.
TAH Turbines designed for earthbound use will run cooler (?; would lower the efficiency) and are built sturdier.
Steam:
Waste heat from most all [continuous service] gas turbines is recoverd as steam.
Adding auxilliary natural gas firing will increase steaming capacity.
Gas turbine temperatures are limited at least for NOx control . . .
and that leaves enough O2 to allow nat gas firing without additional combustion air.
p376 "Combined cycle" system generates additional power from a steam turbine that is driven by gas-turbine-waste-heat steam.
This cuts the overall heat rate to 8,000-8,500 Btu / KWH.
Allow for turbine outages by having 2 gas turbines feeding into the aux-burner waste-heat-recovery section.

package boiler

Used with steam turbine.
Gas turbine exhaust includes an auxilliary burner to increase steam generation over that from gas turbine waste heat.
Steam reformer that is part of either the ammonia or methanol plants includes aux burners, too.
<u>Average</u> steam-to-natgas efficiency is greater in an aux burner than a package boiler
since heat losses are already charged to the process that the aux burner is a part of.
Efficiency of incremental firing is roughly the same in both boilers. TAH 8/31/04

Calculations here are set up to calculate power output after specifying steam flows in & out.
This is because the TG's & boiler's serve the complex.
A power utility would specify power & all steam outflows, then calculate the steam feed requirement.
Based on Uncle Sam's TG performance curves:

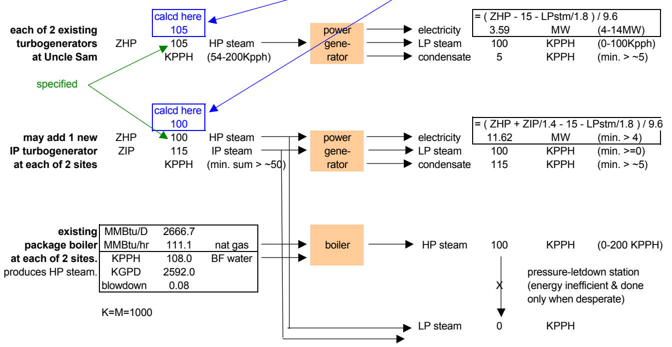
600# kpph in = 15. kpph + 9.6 kpph * MW + 125# kpph out / 1.4 + 40# kpph out / 1.8 + 10# kpph / 2.5

The 1.4, 1.8, & 2.5 constants are the ratio of second-law 'activity coefficient' (if I remember correctly) for these steams vs the feed steam.
The 15 kpph represents friction losses for 1 ~12MW TG.

Power Generation

Tom Hertwig 3/1/00

HP steam requirement, KPPH = 15 + MW * 9.6 + LPsteamOut/1.8



capital
$ MM

0 Power is worth $35 / MWH
So its LP-steam-equivalent is worth:
= $35 / MWH
/ 9.6 Mlb HP steam / MWH
x 1.0 lb HP steam / 1.8 lb LP steam
$2.03 / Mlb LP steam

= 18 * (MWIP/30)^0.6
= 5.91 + 0.407*MW

0 op [nat gas] cost =
= 1K lb steam
x 1000 steam Btu / lb steam
x 1 gas Btu / 0.9 steam Btu
x $4 / gas MMBtu
= $4/0.9 = $4.44/Klb HP steam

0

MW	1997 $MM	model	model % error
30	18.00	18.12	0.67
29	17.64	17.713	0.43
28	17.27	17.306	0.21
27	16.90	16.899	0.01
26	16.52	16.492	-0.16
25	16.13	16.085	-0.31
24	15.74	15.678	-0.42
23	15.35	15.271	-0.50
22	14.94	14.864	-0.53
21	14.53	14.457	-0.52
20	14.11	14.05	-0.45
19	13.69	13.643	-0.31
18	13.25	13.236	-0.09
17	12.80	12.829	0.21
16	12.34	12.422	0.63
15	11.88	12.015	1.17

	0.406846	5.914382
	0.004071	0.09351
	0.9986	0.075074
F	9985.323	14
	56.27809	0.078905

$MM = 5.91+0.407*MW

Sum of LP steam extracted from all turbogenerators = LP steam demand by all the evaporators - SP steam provided by all the sulfuric plants.

HP steam available to all the turbogenerators = HP steam provided by all the sulfuric plants.

IP steam available to the new turbogenerators = IP steam provided by all the new HRS's.

phosphate rock production
~ **CaF2-3Ca3(PO4)2**, a fluoroapatite.

central Florida
North Carolina
Idaho
Morocco
other African countries

Shreve p 270 **phosphate rock [strip] mining**
TAH Need to somehow limit Fe, Al, & especially Mg contaminations to levels (after blending) that minimize need for N-enhancers in making DAP.
Giant draglines strip over-burden, placing it to the side, usually in a mined-out area.
Then the dragline digs the phosphate rock matrix and dumps it in a pit . . .
where the rock is slurried by giant water jets for pumping to a beneficiation plant miles away.
The dragline operator judges what is good matrix by its color and texture . . .
as he is educated by a geologist who has analyzed core samples in the area.

Shreve p 270-3 **phosphate rock beneficiation**
The first step is the washer that produces pebble product, flotation feed, & slimes waste (clay)
Flotation produces concentrate and tailings waste (sand, etc.)

Pebble & concentrate are the 2 parts of the blended phosphate rock product.
Each part has different characteristics and blending is often done custom for each customer.

Sand removed goes to reclaim old strip mines.
Slimes (clay) removed goes to large settling ponds where I believe it stays forever.
TAH Clay fractions carry much phosphate for which there is not an economical recovery process today. OPPORTUNITY.
It often takes acres and years to dewater up to 25% solids -- a major land-management problem.
Shreve (1984) p 272 says "The phosphate industry currently disposes of 60% of these wastes . . .
below ground level and is reclaiming mined-out land."
I believe "below ground" has to mean "landfill" and can't mean "injection wells".
I know that the sandy wastes from beneficiation is definitely used for filling in old mine sites.
Clay ponds are actually above-ground. Levees are raised over the years as the clay accumulates.

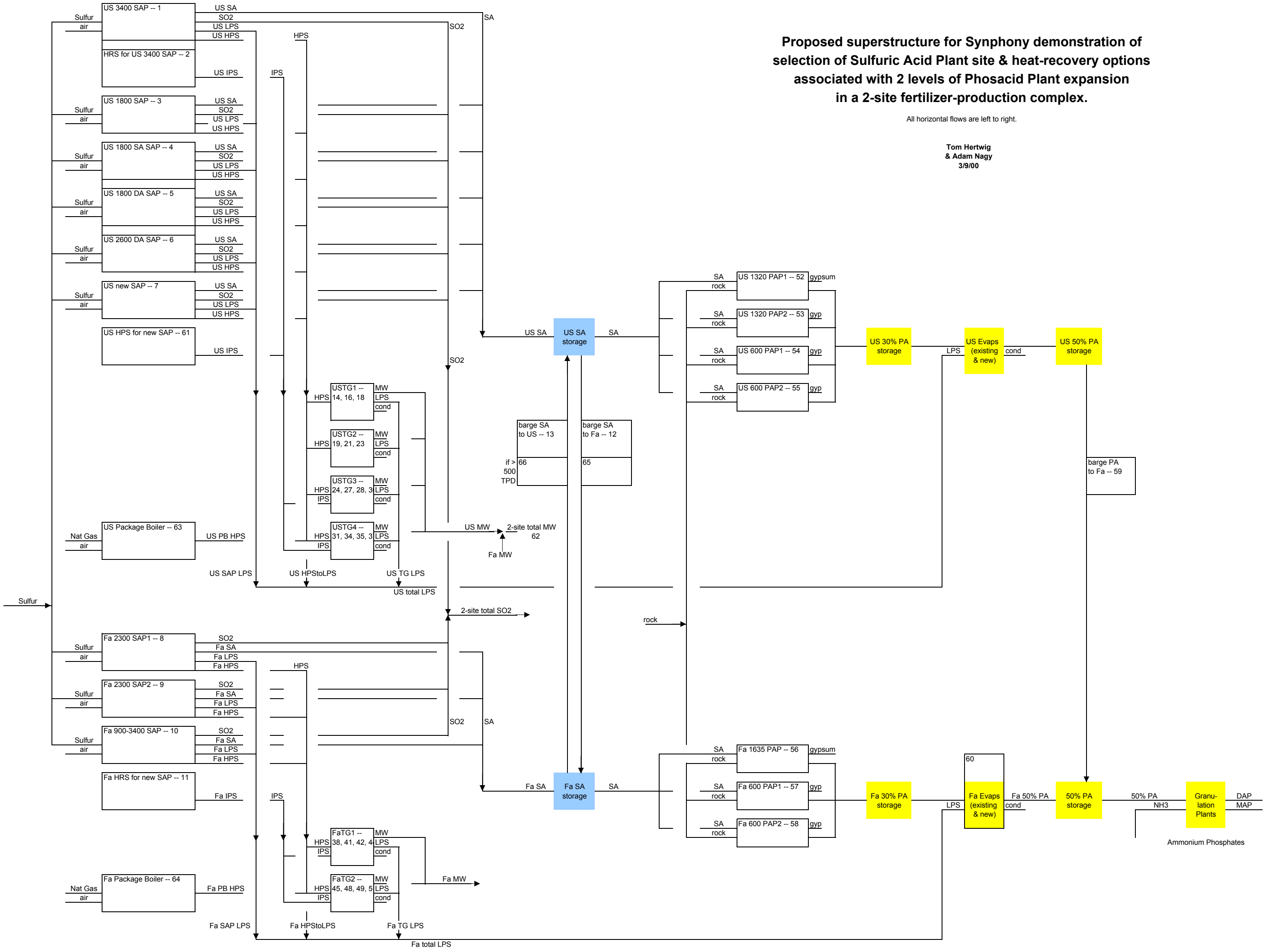
Rock purity is measured as BPL or Bone Phosphate of Lime or % pure Ca3(PO4)2.
Phosphate concentration in rock, acid, or fertilizers is usually referred to on its anhydrous basis, % P2O5.
100%H3PO4 would be (100% x 142/(2x98)=) 72.4% P2O5.

Shreve p274 Since byproducts are not removed when making SuperPhosphates, ...
there a high-purity rock is needed to make grade. Typically use 70-75 BPL.
TAH MAP & DAP are usually made from (50-)55-68 BPL rock.
TAH "Higher PBL" means "lower impurities" BUT says nothing about the types of impurities remaining.
Sand and Ca impurities are easily removed in the phosacid production process:
Sand either is filtered out or is volatilized as SiF4 & scrubbed into gypsum pond water or into salable H2SiF6.
CaCO3 + H2SO4 --> gypsum crystals that are filtered out + CO2 gas that is released to the atmosphere.
CO2 evolution does cause the phosacid to foam, and defoamer must be added to control the foam.
A higher-than-normal CaO-to-P2O5 ratio indicates extra CaCO3 or CaF2.
The stoichiometric ratios are:
120x(56/40) / (62x(142/62)) = 1.183 for Ca3(PO4)2
(40+3x120)x(56/40) / (62x(142/62)) = 1.315 for CaF2-3Ca3(PO4)2, fluorapatite.
Each different rock sample has a slightly different F content, so an actual ratio is only a rough indicator of CO2 evolution.
Fe, Al, & Mg are soluble in 28% P2O5, so they carry on through to ammoniation. These 3 metals, and especially Mg, :
will increase phosacid's viscosity to reduce the all-important gypsum-filtration rates.
will form insoluble phosphates that are not readily available as crop nutrients.
will dilute the fertilizer products, often enough (for DAP) to require N-boosters to meet product N spec.

Proposed superstructure for Synphony demonstration of selection of Sulfuric Acid Plant site & heat-recovery options associated with 2 levels of Phosacid Plant expansion in a 2-site fertilizer-production complex.

All horizontal flows are left to right.

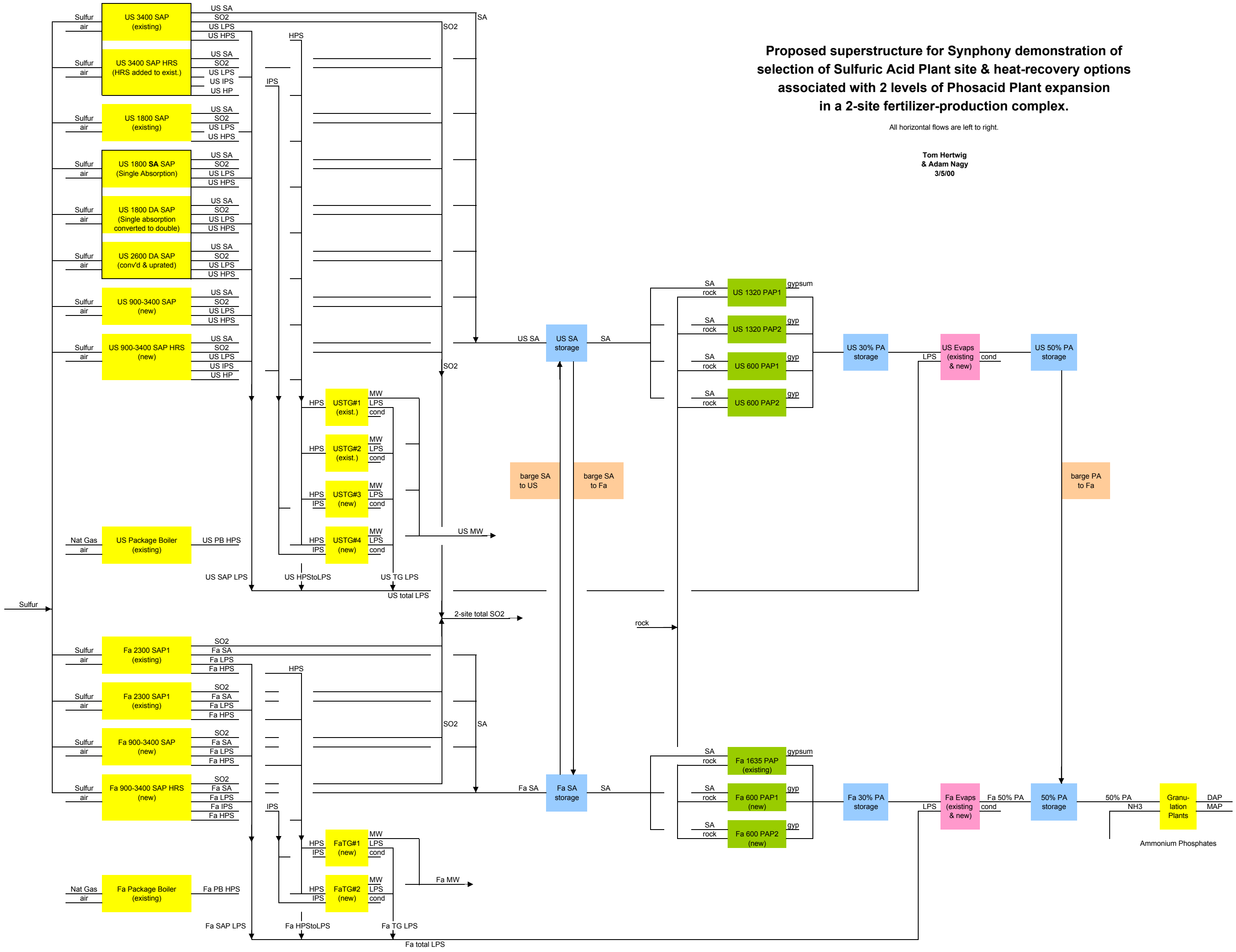
Tom Hertwig
& Adam Nagy
3/9/00



Proposed superstructure for Synphony demonstration of selection of Sulfuric Acid Plant site & heat-recovery options associated with 2 levels of Phosacid Plant expansion in a 2-site fertilizer-production complex.

All horizontal flows are left to right.

Tom Hertwig
& Adam Nagy
3/5/00



wet-process phosphoric acid
alternate processes

hemi-hydrate process:

PCS Nitrogen, Geismar

In a modification of the standard Attack & Filtration process, CaSO4-o.5H2O or hemi-hydrate is deliberately formed.

The hemi is filtered & recrystallized to di-hydrate which is removed on a 2d filter.

The advantage of this process is that acid can be produced at ~40% P2O5 vs 28% in the standard process.

Why? I presume filtration is faster at the higher temps? But the finer hemi- would slow filtration???

This extra strength saves ___% of steam usage in evaporation. This is valuable where extra steam has value, especially to sell or at least displace purchase of electrical power.

The extra strength may make solvent extraction impractical since solids clarification & aqueous/organic phase disengagement times are so long with the extra viscosity.

The re-crystallization improves P2O5 recovery (??) and gypsum purity. Little (??) extra cleanup is needed to make this useable for wallboard.

Wallboard is why phosacid is made from the hemi-hydrate process in Japan where there are no natural gypsum deposits.

solvent extraction

Rhodia, Geismar (food-grade phosphates)

IMC-Agrico (uranium, Uncle Sam & Faustina Plants -- both facilities ran 20 years but are now dismantled due to low uranium prices)

Potential products are Uranium / U3O8 / yellow cake & food-grade phosphates.

Formation of interfacial "crud" at the aqueous-organic interface is a major process consideration.

Need to minimize crud formation by using low-humates rock or by clarifying the feed acid of solids & humates AND/OR develop means to handle the crud formed.

Extraction & stripping coefficients are noticeably sensitive to the acid's P2O5 concentration & temperature, & the solvent's active ingredient concentration [ratio].

So far, solvent extraction uses nominal 28% P2O5. Low phase-disengagement rates, etc. preclude use of ~40% P2O5 as from a hemi-hydrate phosacid process.

The 1970's & '80's uranium extraction processes are essentially 1950's Oak Ridge technology.

Shreve p 273-6 rock digestion with other acids

including phosacid to make GTSP

wet-process phosphoric acid
evaporation & clarification

IMC-Agrico, Uncle Sam & Faustina Plants
PCS Nitrogen, Geismar

Evaporation is needed:
- To allow flexibility in controlling SpGr's in the granulation process where the phosacid is ammoniated.
- To force more CaSO4 out of solution for removal by clarification.
- To make productive use of waste-heat steam (and ?? to minimize natural gas needed to dry granulation products).

Clarification is needed:
- To remove solids that are diluents in the final ammonium phosphate products.
  - Diluent control is critical since product assay standards are set by the world market.
    - Over-grade material earns no better price and under-grade material draws complaints and demands for rebates.
    - Sulfuric acid (-->ammonium sulfate) & urea or ammonium nitrate are often added to DAP to boost N to 18.0%.
  - When starting with Florida phosphate rock, grade control is often difficult; more so for DAP than for MAP.
  - Many African rock sources are enough cleaner that DAP is easily made without N-boosters.
- To remove solids for shipments of "merchant" phosacid.
  - To minimize problems with solids settling in-transit
    - For short-range barging, solids are usually suspended by agitation.
    - Polymer is often added to railcars to make the solids more likely to flow with the acid at unloading.
  - To minimize transportation cost. For this same reason, merchant acid is usually evaporated to a higher strength like

Clarification is done:
- In decreasing priority (including for effectiveness), at nominal 40% P2O5, 30%, then 50%.
- Traditionally use a gravity-based clarifier. Centrifuges are sometimes used, though operating and maintenance costs are
- Where clarification is very needed but marginal, polymeric flocculants are usually added with noticeable benefit.

Clarification is done somewhere between 38 & 43% P2O5 in the evaporator train. The exact point is selected based on trade
- Settling rates decrease as viscosity increases with increasing P2O5 concentration.
- More CaSO4 precipitates with increasing P2O5 concentration.
- Above ~42%P2O5, the precipitates include increasing amounts of P2O5.
  - Sent to the gypsum pond, these P2O5 solids are lost with little chance of being re-dissolved in the pond water for rec
- Choices are limited by:
  - Number of evaporators available.
  - Current capacities of evaporators available.
  - Allowed swings in final evaporator product strength.

fluosilicic acid
H2SiF6

IMC-Agrico, Uncle Sam (& South Pierce, FL) Plants

Phosphate rock is actually a fluorapatite, roughly CaF2-3Ca3(PO4)2.
The fluorine is liberated as fluoride during digestion:
added 7/28/00 (0) CaF2-3Ca3(PO4)2 + 10 H2SO4 + 20 H2O --> 10 CaSO4-2H2O + 2 H3PO4 + 2 HF

In an acid (phosacid), the F- becomes HF which is both a strong acid and a volatile species.
(1) 6HF + SiO2 = H2SiF6 + 2 H2O — Reaction with small amounts of fine sand present in feed rock. Most domestic rock has an excess of SiO2 vs F.
(2) H2SiF6 = SiF4 + 2 HF — Heating under vacuum in an evaporator (or addition of strong acid like H2SO4) will shift reaction to the right.
(3) 3SiF4 + 2H2O = 2H2SiF6 + SiO2 — Scrubbing reaction produces 1 mole of SiO2 that will precipitate . . . .
(1) 6HF + SiO2 = H2SiF6 + 2 H2O — UNLESS there are 6 more moles of HF present to react with it to form 1 more mole of H2SiF6 via reaction (1).

added 7/28/00 Reactions (0) & (1) give a theoretical H2SiF6 production of (1 H2SiF6 @ 144MW / 6 HF @ 20 MW) x (2 HF @ 20MW / 2 H3PO4 @ 98 MW)
added 7/28/00 x (2 H3PO4 @ 98 MW / 1 P2O5 @ 142 MW) = 0.338 T of H2SiF6 generated / T of P2O5 digested
added 7/28/00 However:
added 7/28/00 Not all of the F values in digestion report to the evaporator vapors -- not sure what fraction is available there / tah.
added 7/28/00 Not all evaporator vapors get scrubbed.
added 7/28/00 Not all of the F values in the evaporator vapors get recovered.
added 7/28/00 Demand for H2SiF6 has never been great enough to encourage recovery improvements.
added 7/28/00 With all this, only about 0.024 T of H2SiF6 was recovered / T of P2O5 produced.
added 7/28/00 This gives a rough recovery of only (0.024/0.338=) 6%.

added 7/28/00 Assume H2SiF6 production capacity is available up to 0.024 T H2SiF6 / T of P2O5 produced.
added 7/28/00 H2SiF6 production capacity is added up to this amount by adding a fluorine scrubber to each of the phosacid evaporators whose product strength is above 35% P2O5.
added 7/28/00 Additional H2SiF6 production capacity would require process changes that are not in commercial practice yet.
added 7/28/00 These changes mostly relate to adding more HF to the scrubbing system to control scaling -- as discussed below.

Evaporator vapors MUST be scrubbed of SiF4 & HF **IF** evaporators' barometric condensers use once-through cooling water that discharges to public waters.
When the scrubber liquor is to be sold to fluoridate public drinking water:
- Fresh water is used for makeup.
- The liquor is kept at 20-28% H2SiF6. SiF4-scrubbing efficiency diminishes with H2SiF6 strength and is nil above ~~32% H2SiF6.

Else gypsum pond water is used for scrubbing.
- As with all closed-loop cooling-water systems, the H2SiF6=SiF4+2HF stays in the gypsum pond water.
  - Fluorine accumulation in the pond is limited by use of pond water in digestion, by precipitation of SiF6- salts, & by air emissions.
- This has limited application (eg just the lower-%P2O5 evaporator stages) else it would be easier to convert the barometric condensers to pond water.
  - A cooling tower could NOT be used since it would promote release of fluorine to the air. Scaling & corrosion would also be problems in a cooling tower.
- This is also a useful way to heat filter-wash water.

Control of SiO2 fouling in fluorine scrubbers:
- SiF4 is less soluble in phosacid than HF is, so when evaporators are staged:
  - SiF4 is liberated 1st & mostly between ~35 & ~48% P2O5 / TAH
  - HF is liberated 2nd & mostly between ~40+ & ~54% P2O4 / TAH
- To keep SiO2 from the scrubber reaction (3) from fouling the scrubber, extra HF must be provided.
  - rev'd 7/28/00 Raise evaporator product (%P2O5) strength to raise the incremental HF-to-SiF4 release ratio.
  - added 7/28/00 Raise H2SiF6 strength to decrease SiF4's solubility (& therefore recovery) relative to HF.
  - Somehow add HF to the scrubber H2SiF6.
- Commercial Fluosilicic Acid for treating drinking water:
  - Must have some HF to keep SiO2 from precipitating and clogging feeding pumps.
  - rev'd 7/28/00 Must be <= 1% HF per NSF standards. One plant's typical value was 0.5%.

Since fluorine fumes are irritating, they are drawn from the attack tank & filter & are scrubbed with water.
- This amount of scrubbed fluorine has been permitted for discharge into major rivers.
- In closed-cooling-water plants, gypsum pond water is used to successfully scrub fluorine fumes from process equipment, including from evaporator vapors.
  - Using water already partially saturated with fluorine just requires greater water flows to scrub the same pounds of fluorine.

Fluosilicic Acid Producton

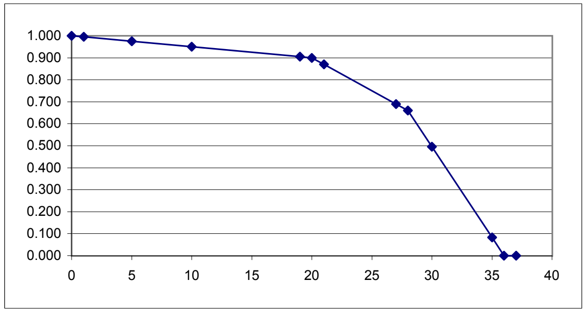
Tom Hertwig 2/23/00

		gross lb/hr	net lb/hr
evap vapors	SiF4	100	91.0
makeup water	H2O	490	490.0
evap vapors	HF	35.6	35.0

HF	
stoich.	35.0
reacted	35.0
excess	0.6

	lb/hr	concentration calculated	concentration min.	concentration max.
SiF4	9.0			
SiO2	0.0		0.0	0.0
H2O	500.5	0.798		
H2SiF6	126.0	0.201	0.20	0.30
HF	0.6	0.0010	0.0010	0.01
acid	627.1	1.000		

% H2SiF6	TAH wag F-recovery			selected
0	1.000	1.5	2.97	1.000
1	0.995	1.47	2.8875	0.995
5	0.975	1.35	2.5575	0.975
10	0.950	1.2	2.145	0.950
19	0.905	0.93	1.4025	0.905
20	0.900	0.9	1.32	0.900
21	0.895	0.87	1.2375	0.870
27	0.865	0.69	0.7425	0.690
28	0.860	0.66	0.66	0.660
30	0.850	0.6	0.495	0.495
35	0.825	0.45	0.0825	0.083
36	0.820	0.42	0	0.000
37	0.815	0.39	-0.0825	0.000



ammonia
NH3
82-0-0

IMC-Agrico, Faustina Plant
CF Industries, Donaldsonville
Triad Nitrogen, Donaldsonville
BCP, Geismar
PCS Nitrogen, Geismar
Monsanto, Luling
Cytec, Westwego (another NH3 plant on-site was converted to MeOH prod'n)

H2 from steam reforming
o.5 N2(g) + 1.5 H2(g) = NH3(g)   DH (12oC) = -46.0 kJ   DH(659oC) = -55.6 kJ
equilibrium constant Kp = p(NH3) / (p(N2)o.5 x p(H2)1.5)
Shreve p304   higher pressure helps converson
(eq vs T&P) charts p306   higher temperature helps kinetics but hurts equilibrium
commercial processes balance kinetics vs equilibrium to minimize sum of equipment & operating costs.
TAH   Have to add a trace of water to product (liquid only?) NH3 to keep it from corroding steel.

Shreve p307   steam-to-ammonia production ratio is 4:1
p309   alternate products = anhydrous gas, anhydrous liquid, & aqueous
each with different temp, press, & volume requirements for storage
and energy requirements in-process.
p309   energy consumption [as natural gas &/or steam]:
1984 typical was 40-45GJ / metric ton of NH3 produced
theoretical minimum of 21GJ / metric ton of NH3 produced
for a higher investment, plant designs are available for 27GJ / metric ton of NH3 produced

Synthesis gas preparation: as written for MeOH
CH4 + H2O -(catalyst)-> CO + 3H2   steam reforming
Reaction is favored by high temp (very endothermic) & low press (no. moles doubles)
p94   ((C + H2O --> CO + H2   ΔH(1000oC) = +135.7 MJ/kg mol   NOTE C=/=CH4 !))

When the final product is CO2, excess steam is used to prevent carbon formation & to force the reaction to completion (via equilibrium constant).
In making CO to make MeOH, steam addition must be carefully controlled to minimize CO2 formation by the water-gas shift reaction:
(CO + H2O -(catalyst usually)-> CO2 + H2   water-gas shift reaction; done in NH3 plant but NOT in MeOH plant)
Reaction is favored by low temp (mildly exothermic) & is unaffected by press.
p94   ΔH(1000oC) = -32.18 MJ/kg mol
Excess steam is used to force the reaction to completion (via equilibrium constant).
In the NH3 plant, this reaction occurs with reforming in the primary reformer that operates at 760-980oC.
Product composition depends on process conditions:
Temp, press, & excess steam determine equilibrium.
Velocity through the catalyst bed determines approach to equilibrium.
Typical product is 75% H2, 8% CO, 15% CO2, 2% balance = N2 + CH4.
Additional cooling & steam is provided to finish converting CO to CO2. In the shift converters AFTER the secondary reformer where air is introduced to get NH3's "N".
CH4 + 2O2 --> CO2 + 2H2O   secondary reformer
1500# steam is produced from this highly exothermic reaction.
Perry 4 p 3-142   ΔH(25oC & gas H2O product) = 21,502. Btu/lb = 191.759 Kcal/gmole
p94   ((C + air --> CO2 + N2   ΔH(1000oC) = -395.4 MJ/kg mol   NOTE C=/=CH4 !))
Air is introduced in the secondary reformer to get NH3's "N" into the process
& [per tah] to complete the oxidation of CO to CO2 for removal with amines.
Perry 4 p 3-142   CO + o.5 O2 --> CO2   ΔH(25oC) = 4343.6 Btu/lb = 67.6361 Kcal/gmole
TAH: Which of O2 vs H2O is more likely to oxidize CO ??? O2 is already busy oxidizing CH4.

p309	Combination of H_2 purification & feed of purified N_2 can eliminate air feed & sec reformer; cuts inerts purge & steam production
	Since CO interferes(?) with ~~shift~~ syngas(tah 5/2/00) converter catalyst, the trace of CO left is converted back to CH_4 in a methanator.
	CH_4 + o.5O_2 --> CO + 2H_2O partial oxidation
	This partial oxidation is needed to cut the H_2:CO ratio from 3.0 for steam reforming to the 2.0 needed to make MeOH. / TAH
	The inerts purge will keep the goal ratio from being an exact integer / TAH.
	ALTERNATELY, the extra CO might (???) be supplied by an ammonia plant . . . but they normally have CO_2 as a byproduct vs CO …
p763	Economical preparation of syngas is vitally important for its cost = 75% of final cost of MeOH.
	Both HP & LP partial oxidation proceses are used.
Synthesis gas p 95-97	Both CO & H_2 come from synthesis gas (steam reforming / TAH).
	[MeOH] synthesis pressure = ~3 MPa (vs ~8 MPa in earlier years).
	Can now use centrifugal compressors. Must cool to remove heat of compression to control converter temp.
p764, p93, p307	Because the [syngas?] catalyst is sensitive to sulfur, sulfur must be removed from the syngas (vs from nat gas feed to syngas prep?).
	Several sulfur-removal processes are available.
	Traditional process uses an aqueous solution of MEA or MDEA to scrub the gas.
p93	Alternate solvents vary in selectivity for absorption of H_2S vs CO_2.
p94	Membrane separation processes are also used. These typically have lower energy & capital costs.
p92	Raw natural gas can contain up to 35g/m3 of H_2S
p307	Sulfur [& Cl] is removed sacrificially in the first [CO-->CO_2 shift /] guard catalyst bed

From Continental Controls, Inc's MVC V3.0 Product Description:

- Operating Objectives:
  - NH_3, CO_2, steam revenues vs fuel & feed gas costs
  - operation of shift converters & synthesis loop to maximize conversion of feedstocks to end products
  - operation of CO_2-removal system to save amine regeneration energy
  - improve plant stability, responsiveness, & safety especially during upsets & disturbances
- Overall Variables:
  - prices for natural gas feed & NH_3 product
    - depend on ag supply & demand
    - weather
    - world economy
  - capacity & throughput limitations
  - variability of gas feedstock quality & composition
  - environmental limitations
  - equipment limitations
- Operating Variables:
  - optimum production rate
  - steam-to-carbon ratio at primary reformer
  - inert gas concentraton in systhesis loop at the ammonia converter inlet
  - H-to-N ratio in synthesis gas
  - primary reformer exit temperature
  - optimim feed gas rate
- Hydraulic model manipulated variables:
  - steam flow to primary reformer
  - purge gas flow
  - feed gas flow
  - synthesis gas compressor LP case inlet pressure
  - header pressure of medium pressure steam system
- Main controlled variables:
  - steam-to-carbon ratio in primary reformer
  - inert gas composition at the ammonia converter inlet
  - front-end pressure
  - feed gas flow to primary reformer
- Secondary reformer model manipulated variables:
  - air rate
  - air compressor speed
- Shift/methanator model manipulated variables:
  - high temperature shift converter inlet temperature
  - shift guard bed inlet temperature (if the unit ixists)
  - low temperature shift converter inlet temperature
  - methanator inlet temperature
- Carbon Dioxide removal manipulated variables:
  - stripping steam rate
  - MDEAmine circulation rate

urea (a simple ideal complex process / tah)
NH2 CO NH2 or CO(NH2)2
46-0-0

IMC-Agrico, Faustina Plant   (plant now down)
CF Industries, Donaldsonville
BCP, Geismar
PCS Nitrogen, Geismar
Cytec, Westwego

46% N; prills or granules; additives can slow storage decomposition losses (to CO2 & NH3) over several months.
Shreve p312 raw material for melamine, resin, plastics, adhesives, coatings, textile anti-shrink ageents, . . .
    ion-exchange resin, ammonium sulfamate, sulfamic acid, pthalocyanines.
CO2 + 2NH3 --(14MPa, 180oC)--> NH2COONH4 = Ammonium Carbamate   DH = -155 MJ/kg-mol
NH2COONH4 = NH2CONH2 + H2O   DH = +42 MJ/kg-mol
Both are equilibrium reactions.
Carbamate formation goes to virtual completion. 14 MPa at 170-190oC Must heat (& pressurize?) to get reaction.
    Most of heat of reaction goes into steam production.
Decomposition to urea is slow & less complete. Driven by heat & pressure reduction. Done in 1 or more decomposers at progressively lower pressures.
Part of this heat comes from the heat of forming the carbamate. *Actually the heat is taken out of the CO2 on its way to the reactor. ????????*
Conversion of either reactant is helped by using an excess of the other reactant (NH3 & CO2).
    (So I'd use excess CO2 to assure conversion of NH3, the more-regulated of the 2 feeds as an emission. / TAH)
Unconverted CO2 & NH3 & undecomposed Carbamate are recovered & recycled. This is a troublesome step.
    All evolved gases must be repressurized to reactor press & this is expensive.
    Old processes were once-through with NH3 to byproducts or partial recycle. Only total-recycle is considered today
Synthesis is further complicated by formation of a dimer called biuret, NH2CONHCONH2-2H2O, which adversely affects the growth of some plants.
Decomposer product is a urea solution that must be evaporated to be prilled or granulated.
    Heat the solution to release unreacted gases & undecomposed carbamate.
    Evaporate with ~50# steam. Vapors include some NH3. Could scrub or use recent XXX stripper process to recycle to NH3 plant (??).
    Granulate (or prill = older standard process).
Overall, 99+% of both CO2 & NH3 are converted to urea, making environmental problems minimal.
Air is introduced into the process with the CO2 for air's O2 to let 300 series stainless steels . . .
    resist carbamate that is otherwise very corrosive to ordinary & stainless steels.

TAH Product urea decomposes to CO2 & NH3 over months, but can be slowed by various additives (coatings? including formaldehyde!)
TAH   Formaldehyde is reacted, leaving no liability in the product urea.

Urea MW = 60.06
Ammonia MW = 17.03   0.567
N MW is 14.01   0.467
so urea is 46.7%N & 56.7 T NH3 is needed to produce 100 T urea.
CO2 MW = 44.01   0.733
so 73.3 T CO2 is needed to produce 100 T urea.

Mono-/Di- Ammonium Phosphates (MAP/DAP)
NH4 H2PO4 / (NH4)2 HPO4

Ammonium phosphate fertilizers are not close to pure and standard grades are:

… 18-46-0 (18%N - 46%P2O5 - 0%K2O) which corresponds to 1.73 N/P mole ratio vs 2.00 if a true "di-"
10-50-0 = 0.90 ratio
10-52-0 = 0.85
… 11-52-0 = 0.94

Product reactions:

H3PO4 + NH3 --> NH4 H2PO4 MAP
NH4 H2PO4 + NH3 --> (NH4)2 HPO4 DAP

Scrubber reactions:

Need to capture unreacted NH3 & Fluorides:
Per permit limits -- though it is not yet feasible to measure these losses on a continuous basis.
To prevent NH3-smell complaints from plant neighbors.
To prevent 2NH3 + H2O + SO2 from sulfuric plant stacks --> (NH4)2SO3, a white haze
H3PO4 + NH3 --> NH4 H2PO4 capture NH3; permit limits last-stage scrubber pH to __-__ to maximize NH3(??) capture.
NH3 + HF --> NH4F capture HF; (how assured??)
TAH fabrication: 4NH3 + 3SiF4 + 2H2O --> 2(NH4)2SiF6 + SiO2 capture SiF4; uncaptured SiF4 --> haze of H2SiF6 mist &/or SiO2 particles

AM + PA = 100
AM tons of 14/17 N = 100 tons of 18-46-0 DAP x 0.18

Process feeds are: PA tons of 100% P2O5 = 100 tons of 18-46-0 DAP x 0.46

Anhydrous NH3 (liquid &/or vapor) AM = 18 x 17/14 = 21.857
Phosacid at 40-54% P2O5 PA = 46
a basis for cx opt'n --> May also feed unevaporated phosacid at ~28% P2O5 when evaporation capacity is not available. Displaces 50% P2O5 & makeup water.
Water for scrubber SpGr control & to use up old process-wash water.
Inventory of this "pond" water varies with wash frequency & rainfall.
Outside water is used only when DAP-pond water is not available.
"Outside water" is gyp-pond water first and fresh water second.
N boosters:
H2SO4 + 2NH3 = (NH4)2SO4
NH2 CO NH2 (urea, granular or solution)
(NH3)2NO3 (AN, granular or solution)

Ammoniation is done in stages:

Done first in the scrubbers where NH3 recovery is emphasized.
Done as much as possible in liquid phase where ammoniation is most efficient.
Create a solid product only in the final stage.
The 2 liquid feeds are applied to recycled granules to grow the granules.
Solids formed elsewhere due to poor control, etc. will accumulate leading to plugged equipment, fumes, & downtime.

* * * * * * **Process concerns** -- none of which seem subject to an optimization model, except perhaps the scrubbing process design.
Making product spec assay & size -- a function of operator skills & process controls.
NH3 recovery -- a function of scrubber operating conditions and fouling. And of the scrubbing process design.
Natural gas volume needed to dry the product -- a function of urea & gypsum contents, operator skills, & process controls.
Urea is hygroscopic, making the DAP product all the more difficult to dry.
To the extent that the DAP product contains gypsum, the DAP is harder to "dry" --
-- IF you need to drive out gypsum's water of hydration to make product-spec assay.
Perry 4 p3-8 Gypsum loses 1.5 waters of hydration by 262oF & all 2.0 waters by 325oF. (128 & 163 oC)
Process temperatures need to be limited to minimize release/loss of NH3.
Pure MAP/DAP do not decompose, but any trapped NH3 can be driven out before having a last chance to react.
N-booster urea is especially sensitive to temperature (&time).
Perry 4 p3-42 Urea melts at 271oF and decomposes instead of boiling.
Typically "half" of the N value in urea is released as NH3 in the DAP process.
This reduces urea's advantage over NH3 in boosting %N.

Evaporation is needed:
To allow flexibility in controlling SpGr's in the granulation process where the phosacid is ammoniated.
To force more CaSO4 out of solution for removal by clarification.
To make productive use of waste-heat steam (and ?? to minimize natural gas needed to dry granulation products).

Clarification is needed:
To remove solids that are diluents in the final ammonium phosphate products.
Diluent control is critical since product assay standards are set by the world market.
Over-grade material earns no better price and under-grade material draws complaints and demands for rebates.
Sulfuric acid (-->ammonium sulfate) & urea or ammonium nitrate are often added to DAP to boost N to 18.0%.
When starting with Florida phosphate rock, grade control is often difficult; more so for DAP than for MAP.
Many African rock sources are enough cleaner that DAP is easily made without N-boosters.

di-ammonium phosphate		Faustina & Taft
mono-ammonium phosphate		Faustina
granulat tripple super phosphate		
nitric acid	from NH3	CF Industries
		PCS Nitrogen, Geismar
ammonium nitrate		PCS Nitrogen, Geismar
urea ammonium nitrate solutions		CF Industries
		PCS Nitrogen, Geismar
acetic acid	MeOH + CO	BCP
syngas for H2 & CO (ex-refinery)		Air Products, Geismar (converted NH3 plant; feeds H2 pipiline; CO to BASF)
		Praxair, Geismar (H2 to Exxon, BR & CO to Rubicon for urethane intermediates)
		Some H2 & CO is separated by cryogenic distillation.
oleum		SO3 absorption tower run in parallel to normal-SAP's PAT; just control at different strength.
liq SO3		

acidulating phosphate rock with nitric acid sounds great but the product cakes on storage. Shreve p 313

7/28/00 notes

natural gas usage

MMBtu/T NH3	21.0 for process
	14.7 for fuel
	35.7 total
MMBtu/T DAP	0.2 for dryer fuel
MMBtu/SAP	6000 per reheat x 1 reheat/yr

urea usage as N booster — 0.01 T urea / T DAP
0 for MAP

H2SO4 usage in Ammonium Phosphates as N booster
0.014 T H2SO4 / T DAP
0.012 T H2SO4 / T MAP

Florida rock — 1.48 T CaO / T P2O5
rock digestion — 2.72 T H2SO4 / T P2O5 produced
please compare thee values to theoretical relationship.

rock digestion — 0.77 T H2SO4 / T 64BPL rock digested
rock digestion — 3.54 T 64BPL rock / T P2O5 produced.
please compare these values to theoretical relationship that is a function of BPL

7/19/00 notes from
call to Glenn Bryson, BCP
& David Kellings, Haldor-Topsoe

Methanol plants
shutdown plants were 100 & 125 Mgpy
these were the old high-pressure (~5000 psi) processes
first low-pressure processes were built in the late '70's
lower pressure saves operating energy costs.
plants running today run at 700-1500 psi = "low pressure"
new plants would be built at 600-1000 psi

plants are often sized for specific users and so are not always "world-scale" as sulfuric acid plants usually are.
world-scale plants running 10 years ago were 1500-2000-2500 metric TPD .
world-scale plants running today are 2500-3000 metricTPD.
a 5000 metricTPD plant may be in somebody's planning.
BCP's nameplate 574 Mgpy AA grade plant is now run at 900 Mgpd A grade.
rate improvements include:
- H2 recovery from syngas loop purge
- distillation improvements
- better catalysts that allow operation at lower pressures.

assume 6.6 lb MeOH / gal
A grade is ~~98% pure
AA grade is ~~99.5% pure per GB
AA grade is ~99.999% pure per DK
grade is improved with additional distillation
all production today is AA per DK -- does not match GB's current A production.!?!?!?

typical 0.10-0.11 MMBty/gal for process & fuel gas -- (not necessarily natural gas ?)
some plants run <0.10 but they are buying O2 instead

BCP urea plant 800 TPD (short tons?)

BCP NH3 plant 450 TPD uprated to 1200 (short tons?)

APPENDIX D STREAM FLOW RATES AMONG PLANTS IN THE CHEMICAL PRODUCTION COMPLEX

Table D-1 Stream Flow Rates Among Plants, Base Case

Plant Name	Entering Streams	Flow Rate (metric tons/year)	Leaving Streams	Flow Rate (metric tons/year)
Contact process sulfuric acid	Sulfur (S4)	1,190,000	Sulfuric acid (S14)	3,680,000
	Air (S7)	7,680,000	Vent (S15)	5,910,000
	Boiler feed water (S61$_S$)	5,770,000	LP steam (S16$_S$)	1,910,000
	H_2O (S66)	721,000	HP steam (S17$_S$)	2,870,000
			Blowdown (S67$_S$)	415,000
			IP steam (S77$_S$)	575,000
			Others (S803)	1,190
Wet process phosphoric acid	Phosphate rock (S13)	4,520,000	Gypsum (S22)	5,300,000
	Decant water (S21)	2,880,000	H_2SiF_6 solution (S49)	221,000
	LP steam (S24$_S$)	2,360,000	Others (S50)	1,010,000
	Sulfuric acid (S14)	3,680,000	Phosphoric acid (S60)	2,640,000
			Condensed water (S75$_S$)	2,360,000
			H_2O (S420)	1,890,000
GTSP	Phosphate rock (S12)	301,000	GTSP (S51)	749,000
	Phosphoric acid (S39)	503,000	HF (S63)	9,710
	Inert (S74)	124,000	H_2O (S422)	170,000
Ammonia	Air (S9)	720,000	NH_3 (S19)	658,000
	Natural gas (S10)	274,000	CO_2 (S20)	753,000
	Steam (S68)	522,000	H_2O (S69)	93,800
			Purge (S70)	12,100
Nitric acid	Air (S8)	934,000	HNO_3 (S45)	331,000
	NH_3 (S29)	49,200	Vent (S81)	752,000
	H_2O (S71)	99,500		
Urea	LP steam (S27$_S$)	37,400	Granular urea (S46)	74,200
	NH_3 (S31)	56,700	Urea to MAP and DAP (S53)	25,600
	CO_2 (S32)	73,200	H_2O (S53H2O)	29,900
			Condensed water (S65$_S$)	37,400
			NH_3 emission (S800)	57
			CO_2 emission (S801)	73
Methanol	Natural gas (S11)	68,200	Methanol (S47)	181,000
	Steam (S28)	51,100	Purge (S802)	774
	CO_2 (S33)	62,900		
Ammonium nitrate	NH_3 (S44)	48,300	Granular NH_4NO_3 (S56)	218,000
	HNO_3 (S45)	331,000	NH_4NO_3 solution (S62)	27,800
			H_2O to nitric acid(S71)	99,500
			H_2O (S804)	33,100

Table D-1 Continued

Plant Name	Entering Streams	Flow Rate (metric tons/year)	Leaving Streams	Flow Rate (metric tons/year)
MAP and DAP	Phosphoric acid (S40)	2,120,000	MAP (S52)	293,000
	NH_3 (S42)	450,000	DAP (S57)	1,880,000
	Urea (S53)	25,600	H_2O (S76)	714,000
	Inert (S55)	292,000		
UAN	Urea (S54)	32,600	UAN (S58)	60,500
	NH_4NO_3 solution (S62)	27,800		
Power generation	HP steam ($S17_S$)	2,870,000	H_2O (S78)	830,000
	IP steam ($S77_S$)	575,000	LP steam (S18)	3,810,000
	Boiler feed water (Sbf)	1,200,000	CO_2 (S301)	137,000
	Fuel (methane) (S300)	50,000	Electricity (Se1+Se2)	1,779 (TJ)
Acetic acid	CO_2 (S82)	4,490	Acetic acid (S84)	8,160
	CH_4 (S83)	545	H_2O (S425)	1,220
	Methanol (S424)	4,360		
Ethylbenzene	Benzene (S1067)	583,000	Ethylbenzene (S1069)	862,000
	Ethylene (S1068)	228,000		
	Benzene from styrene (S1074)	50,700		
Styrene	Ethylbenzene (S1071)	862,000	Styrene (S1072)	753,000
			Fuel gas (S1073)	35,500
			Benzene (S1074)	50,700
			Toluene (S1075)	6,730
			C (S1076)	15,600

Table D-2 Stream Flow Rates Among Plants in Optimal Structure from Superstructure

Plant Name	Entering Streams	Flow Rate (metric tons/year)	Leaving Streams	Flow Rate (metric tons/year)
Contact process sulfuric acid	Sulfur (S4)	1,190,000	Sulfuric acid (S14)	3,680,000
	Air (S7)	7,680,000	Vent (S15)	5,910,000
	Boiler feed water (S61$_S$)	5,770,000	LP steam (S16$_S$)	1,910,000
	H_2O (S66)	721,000	HP steam (S17$_S$)	2,870,000
			Blowdown (S67$_S$)	415,000
			IP steam (S77$_S$)	575,000
			Others (S803)	1,190
Wet process phosphoric acid	Phosphate rock (S13)	4,520,000	Gypsum (S22)	5,300,000
	Decant water (S21)	2,880,000	H_2SiF_6 solution (S49)	221,000
	LP steam (S24$_S$)	2,360,000	Others (S50)	1,010,000
	Sulfuric acid (S14)	3,680,000	Phosphoric acid (S60)	2,640,000
			Condensed water (S75$_S$)	2,360,000
			H_2O (S420)	1,890,000
GTSP	Phosphate rock (S12)	301,000	GTSP (S51)	749,000
	Phosphoric acid (S39)	503,000	HF (S63)	9,710
	Inert (S74)	124,000	H_2O (S422)	170,000
Ammonia	Air (S9)	720,000	NH_3 (S19)	658,000
	Natural gas (S10)	274,000	CO_2 (S20)	753,000
	Steam (S68)	522,000	H_2O (S69)	93,800
			Purge (S70)	12,100
Nitric acid	Air (S8)	934,000	HNO_3 (S45)	331,000
	NH_3 (S29)	49,200	Vent (S81)	752,000
	H_2O (S71)	99,500		
Urea	LP steam (S27$_S$)	37,400	Granular urea (S46)	74,200
	NH_3 (S31)	56,700	Urea to MAP and DAP (S53)	25,600
	CO_2 (S32)	73,200	H_2O (S53H2O)	29,900
			Condensed water (S65$_S$)	37,400
			NH_3 emission (S800)	57
			CO_2 emission (S801)	73
Methanol	Natural gas (S11)	68,200	Methanol (S47)	181,000
	Steam (S28)	51,100	Purge (S802)	774
	CO_2 (S33)	62,900		
Ammonium nitrate	NH_3 (S44)	48,300	Granular NH_4NO_3 (S56)	218,000
	HNO_3 (S45)	331,000	NH_4NO_3 solution (S62)	27,800
			H_2O to nitric acid(S71)	99,500
			H_2O (S804)	33,100
MAP and DAP	Phosphoric acid (S40)	2,120,000	MAP (S52)	293,000
	NH_3 (S42)	450,000	DAP (S57)	1,880,000
	Urea (S53)	25,600	H_2O (S76)	714,000

Table D-2 Continued

Plant Name	Entering Streams	Flow Rate (metric tons/year)	Leaving Streams	Flow Rate (metric tons/year)
MAP and DAP (Continued)	Inert (S55)	292,000		
UAN	Urea (S54)	32,600	UAN (S58)	60,500
	NH_4NO_3 solution (S62)	27,800		
Power generation	HP steam ($S17_S$)	2,870,000	H_2O (S78)	991,000
	IP steam ($S77_S$)	575,000	LP steam (S18)	5,010,000
	Boiler feed water (Sbf)	2,560,000	CO_2 (S301)	293,000
	Fuel (methane) (S300)	107,000	Electricity (Se1+Se2)	2,270 (TJ)
Ethyl-benzene	Benzene (S1067)	583,000	Ethylbenzene (S1069)	862,000
	Ethylene (S1068)	228,000		
	Benzene from styrene (S1074)	50,700		
Styrene	Ethylbenzene (S1071)	862,000	Styrene (S1072)	753,000
			Fuel gas (S1073)	35,500
			Benzene (S1074)	50,700
			Toluene (S1075)	6,730
			C (S1076)	15,600
New acetic acid	CO_2 (S700)	5,990	Acetic acid (S702)	8,180
	CH_4 (S701)	2,180		
Formic acid	CO_2 (S942)	74,500	Formic acid (S944)	77,900
	Hydrogen (S943)	3,420		
Methyl-amines	CO_2 (S946)	104,000	CO and CO_2 (S949)	6,840
	Hydrogen (S947)	13,400	MMA (S950)	26,400
	NH_3 (S948)	25,400	DMA (S951)	28,800
			H_2O (S952)	80,900
Graphite	CH_4 (S992)	36,700	Hydrogen (S994)	3,000
	CO_2 (S993)	67,900	C (S995)	46,000
			H_2O (S996)	55,600
Hydrogen /Synthesis gas	CH_4 (S934)	42,800	Hydrogen (S936)	10,800
	CO_2 (S935)	117,000	CO (S937)	149,000
Propylene from CO_2	Propane (S911)	43,900	CO (S913)	14,000
	CO_2 (S912)	21,900	Propylene (S914)	41,900
			H_2O (S915)	8,980
			Hydrogen (S916)	1,010
Propylene from propane	Propane (S917)	43,800	Hydrogen (S918)	2,010
			Propylene (S919)	41,800

Table D-3 Stream Flow Rates Among Plants in Optimal Structure from Superstructure, Extension 2 of Previous Work

Plant Name	Entering Streams	Flow Rate (metric tons/year)	Leaving Streams	Flow Rate (metric tons/year)
Contact process sulfuric acid	Sulfur (S4)	1,190,000	Sulfuric acid (S14)	3,680,000
	Air (S7)	7,680,000	Vent (S15)	5,910,000
	Boiler feed water ($S61_S$)	5,770,000	LP steam ($S16_S$)	1,910,000
	H_2O (S66)	721,000	HP steam ($S17_S$)	2,870,000
			Blowdown ($S67_S$)	415,000
			IP steam ($S77_S$)	575,000
			Others (S803)	1,190
Wet process phosphoric acid	Phosphate rock (S13)	4,520,000	Gypsum (S22)	5,300,000
	Decant water (S21)	2,880,000	H_2SiF_6 solution (S49)	221,000
	LP steam ($S24_S$)	2,360,000	Others (S50)	1,010,000
	Sulfuric acid (S14)	3,680,000	Phosphoric acid (S60)	2,640,000
			Condensed water ($S75_S$)	2,360,000
			H_2O (S420)	1,890,000
GTSP	Phosphate rock (S12)	301,000	GTSP (S51)	749,000
	Phosphoric acid (S39)	503,000	HF (S63)	9,710
	Inert (S74)	124,000	H_2O (S422)	170,000
Ammonia	Air (S9)	720,000	NH_3 (S19)	658,000
	Natural gas (S10)	274,000	CO_2 (S20)	753,000
	Steam (S68)	522,000	H_2O (S69)	93,800
			Purge (S70)	12,100
Nitric acid	Air (S8)	934,000	HNO_3 (S45)	331,000
	NH_3 (S29)	49,200	Vent (S81)	752,000
	H_2O (S71)	99,500		
Urea	LP steam ($S27_S$)	37,400	Granular urea (S46)	74,200
	NH_3 (S31)	56,700	Urea to MAP and DAP (S53)	25,600
	CO_2 (S32)	73,200	H_2O (S53H2O)	29,900
			Condensed water ($S65_S$)	37,400
			NH_3 emission (S800)	57
			CO_2 emission (S801)	73
Methanol	Natural gas (S11)	68,200	Methanol (S47)	181,000
	Steam (S28)	51,100	Purge (S802)	774
	CO_2 (S33)	62,900		
Ammonium nitrate	NH_3 (S44)	48,300	Granular NH_4NO_3 (S56)	218,000
	HNO_3 (S45)	331,000	NH_4NO_3 solution (S62)	27,800
			H_2O to nitric acid(S71)	99,500
			H_2O (S804)	33,100
MAP and DAP	Phosphoric acid (S40)	2,120,000	MAP (S52)	293,000
	NH_3 (S42)	450,000	DAP (S57)	1,880,000

Table D-3 Continued

Plant Name	Entering Streams	Flow Rate (metric tons/year)	Leaving Streams	Flow Rate (metric tons/year)
MAP and DAP (Continued)	Urea (S53) Inert (S55)	25,600 292,000	H_2O (S76)	714,000
UAN	Urea (S54) NH_4NO_3 solution (S62)	32,600 27,800	UAN (S58)	60,500
Power generation	HP steam ($S17_S$) IP steam ($S77_S$) Boiler feed water (Sbf) Fuel (methane) (S300)	2,870,000 575,000 1,100,000 46,000	H_2O (S78) LP steam (S18) CO_2 (S301) Electricity (Se1+Se2)	818,000 3,730,000 126,000 1,744 (TJ)
Ethylbenzene	Benzene (S1067) Ethylene (S1068) Benzene from styrene (S1074)	583,000 228,000 50,700	Ethylbenzene (S1069)	862,000
Styrene	Ethylbenzene (S1071)	862,000	Styrene (S1072) Fuel gas (S1073) Benzene (S1074) Toluene (S1075) C (S1076)	753,000 35,500 50,700 6,730 15,600
New acetic acid	CO_2 (S700) CH_4 (S701)	5,990 2,180	Acetic acid (S702)	8,180

Table D-4 Stream Flow Rates Among Plants, Base Case of Extension 3 in Previous Work

Plant Name	Entering Streams	Flow Rate (metric tons/year)	Leaving Streams	Flow Rate (metric tons/year)
Contact process sulfuric acid	Sulfur (S4)	1,190,000	Sulfuric acid (S14)	3,680,000
	Air (S7)	7,680,000	Vent (S15)	5,910,000
	Boiler feed water (S61$_S$)	5,770,000	LP steam (S16$_S$)	1,910,000
	H_2O (S66)	721,000	HP steam (S17$_S$)	2,870,000
			Blowdown (S67$_S$)	415,000
			IP steam (S77$_S$)	575,000
			Others (S803)	1,190
Wet process phosphoric acid	Phosphate rock (S13)	4,520,000	Gypsum (S22)	5,300,000
	Decant water (S21)	2,880,000	H_2SiF_6 solution (S49)	221,000
	LP steam (S24$_S$)	2,360,000	Others (S50)	1,010,000
	Sulfuric acid (S14)	3,680,000	Phosphoric acid (S60)	2,640,000
			Condensed water (S75$_S$)	2,360,000
			H_2O (S420)	1,890,000
GTSP	Phosphate rock (S12)	301,000	GTSP (S51)	749,000
	Phosphoric acid (S39)	503,000	HF (S63)	9,710
	Inert (S74)	124,000	H_2O (S422)	170,000
Ammonia	Air (S9)	720,000	NH_3 (S19)	658,000
	Natural gas (S10)	274,000	CO_2 (S20)	753,000
	Steam (S68)	522,000	H_2O (S69)	93,800
			Purge (S70)	12,100
Nitric acid	Air (S8)	934,000	HNO_3 (S45)	331,000
	NH_3 (S29)	49,200	Vent (S81)	752,000
	H_2O (S71)	99,500		
Urea	LP steam (S27$_S$)	37,400	Granular urea (S46)	74,200
	NH_3 (S31)	56,700	Urea to MAP and DAP (S53)	25,600
	CO_2 (S32)	73,200	H_2O (S53H2O)	29,900
			Condensed water (S65$_S$)	37,400
			NH_3 emission (S800)	57
			CO_2 emission (S801)	73
Methanol	Natural gas (S11)	68,200	Methanol (S47)	181,000
	Steam (S28)	51,100	Purge (S802)	774
	CO_2 (S33)	62,900		
Ammonium nitrate	NH_3 (S44)	48,300	Granular NH_4NO_3 (S56)	218,000
	HNO_3 (S45)	331,000	NH_4NO_3 solution (S62)	27,800
			H_2O to nitric acid(S71)	99,500
			H_2O (S804)	33,100

Table D-4 Continued

Plant Name	Entering Streams	Flow Rate (metric tons/year)	Leaving Streams	Flow Rate (metric tons/year)
MAP and DAP	Phosphoric acid (S40)	2,120,000	MAP (S52)	293,000
	NH_3 (S42)	450,000	DAP (S57)	1,880,000
	Urea (S53)	25,600	H_2O (S76)	714,000
	Inert (S55)	292,000		
UAN	Urea (S54)	32,600	UAN (S58)	60,500
	NH_4NO_3 solution (S62)	27,800		
Power generation	HP steam ($S17_S$)	2,870,000	H_2O (S78)	746,000
	IP steam ($S77_S$)	575,000	LP steam (S18)	3,190,000
	Boiler feed water (Sbf)	491,000	CO_2 (S301)	56,100
	Fuel (methane) (S300)	20,500	Electricity (Se1+Se2)	1,523 (TJ)
Acetic acid	CO_2 (S82)	4,490	Acetic acid (S84)	8,160
	CH_4 (S83)	545	H_2O (S425)	1,220
	Methanol (S424)	4,360		
Sylvinite process KCl	Sylvinite KCl ore (S101)	465,000	KCl (S102)	198,000
			NaCl (S103)	263,000
			Others (S104)	3,260
Solid blend	KCl from sylvinite (S125)	2,850	Solid blend (S140)	10,000
	GTSP (S128)	0		
	MAP (S130)	0		
	DAP (S132)	3,910		
	NH_4NO_3 (S146)	3,130		
	Urea (S150)	0		
	Fillings (S170)	107		
Liquid blend	KCl from sylvinite (S126)	196,000	Liquid blend (S141)	2,060,000
	NH_4NO_3 (S135)	215,000		
	UAN (S137)	60,500		
	Urea (S139)	41,600		
	GTSP (S147)	0		
	MAP (S148)	0		
	DAP (S149)	403,000		
	Fillings (S163)	1,140,000		

Table D-5 Stream Flow Rates Among Plants of Optimal Structure from Superstructure of Extension 3 in Previous Work

Plant Name	Entering Streams	Flow Rate (metric tons/year)	Leaving Streams	Flow Rate (metric tons/year)
Contact process sulfuric acid	Sulfur (S4)	1,190,000	Sulfuric acid (S14)	3,680,000
	Air (S7)	7,680,000	Vent (S15)	5,910,000
	Boiler feed water ($S61_S$)	5,770,000	LP steam ($S16_S$)	1,910,000
	H_2O (S66)	721,000	HP steam ($S17_S$)	2,870,000
			Blowdown ($S67_S$)	415,000
			IP steam ($S77_S$)	575,000
			Others (S803)	1,190
Wet process phosphoric acid	Phosphate rock (S13)	4,520,000	Gypsum (S22)	5,300,000
	Decant water (S21)	2,880,000	H_2SiF_6 solution (S49)	221,000
	LP steam ($S24_S$)	2,360,000	Others (S50)	1,010,000
	Sulfuric acid (S14)	3,680,000	Phosphoric acid (S60)	2,640,000
			Condensed water ($S75_S$)	2,360,000
			H_2O (S420)	1,890,000
GTSP	Phosphate rock (S12)	301,000	GTSP (S51)	749,000
	Phosphoric acid (S39)	503,000	HF (S63)	9,710
	Inert (S74)	124,000	H_2O (S422)	170,000
Ammonia	Air (S9)	720,000	NH_3 (S19)	658,000
	Natural gas (S10)	274,000	CO_2 (S20)	753,000
	Steam (S68)	522,000	H_2O (S69)	93,800
			Purge (S70)	12,100
Nitric acid	Air (S8)	934,000	HNO_3 (S45)	331,000
	NH_3 (S29)	49,200	Vent (S81)	752,000
	H_2O (S71)	99,500		
Urea	LP steam ($S27_S$)	37,400	Granular urea (S46)	74,200
	NH_3 (S31)	56,700	Urea to MAP and DAP (S53)	25,600
	CO_2 (S32)	73,200	H_2O (S53H2O)	29,900
			Condensed water ($S65_S$)	37,400
			NH_3 emission (S800)	57
			CO_2 emission (S801)	73
Methanol	Natural gas (S11)	68,200	Methanol (S47)	181,000
	Steam (S28)	51,100	Purge (S802)	774
	CO_2 (S33)	62,900		
Ammonium nitrate	NH_3 (S44)	48,300	Granular NH_4NO_3 (S56)	218,000
	HNO_3 (S45)	331,000	NH_4NO_3 solution (S62)	27,800
			H_2O to nitric acid(S71)	99,500
			H_2O (S804)	33,100

Table D-5 Continued

Plant Name	Entering Streams	Flow Rate (metric tons/year)	Leaving Streams	Flow Rate (metric tons/year)
MAP and DAP	Phosphoric acid (S40)	2,120,000	MAP (S52)	293,000
	NH_3 (S42)	450,000	DAP (S57)	1,880,000
	Urea (S53)	25,600	H_2O (S76)	714,000
	Inert (S55)	292,000		
UAN	Urea (S54)	32,600	UAN (S58)	60,500
	NH_4NO_3 solution (S62)	27,800		
Power generation	HP steam ($S17_S$)	2,870,000	H_2O (S78)	738,000
	IP steam ($S77_S$)	575,000	LP steam (S18)	3,120,000
	Boiler feed water (Sbf)	419,000	CO_2 (S301)	47,800
	Fuel (methane) (S300)	17,400	Electricity (Se1+Se2)	1,497 (TJ)
Solid blend	KCl from IMC (S122)	2,850	Solid blend (S140)	10,000
	GTSP (S128)	0		
	MAP (S130)	0		
	DAP (S132)	3,910		
	NH_4NO_3 (S146)	3,130		
	Urea (S150)	0		
	Fillings (S170)	107		
Liquid blend	KCl from IMC (S123)	196,000	Liquid blend (S141)	2,060,000
	NH_4NO_3 (S135)	215,000		
	UAN (S137)	60,500		
	Urea (S139)	41,600		
	GTSP (S147)	0		
	MAP (S148)	0		
	DAP (S149)	403,000		
	Fillings (S163)	1,140,000		
New acetic acid	CO_2 (S700)	5,990	Acetic acid (S702)	8,180
	CH_4 (S701)	2,180		
IMC process KCl	KCl ore (S89)	1,250,000	KCl (S90)	198,000
			NaCl (S91)	778,000
			Others (S92)	271,000

VITA

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