DEVELOPMENT AND INTEGRATION OF NEW PROCESSES CONSUMING CARBON DIOXIDE IN MULTI-PLANT CHEMICAL PRODUCTION COMPLEXES

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Sudheer Indala
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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

New, energy-efficient and environmentally acceptable, catalytic processes have been identified that can use excess high purity carbon dioxide as a raw material from synthesis gas and other sources available in a chemical production complex. The chemical production complex in the lower Mississippi River Corridor has been used to show how these new plants can be integrated into this existing infrastructure using the Chemical Complex and Cogeneration Analysis System.

Eighty six published articles of laboratory and pilot plant experiments were reviewed that describe new methods and catalysts to use carbon dioxide for producing commercially important products. Reactions have been categorized as hydrogenation reactions producing alcohols; hydrocarbon synthesis reactions producing paraffins and olefins; amine syntheses producing methyl and higher order amines; and hydrolysis reactions producing alcohols and organic acids. Also carbon dioxide can serve as an oxygen source in the ethylbenzene-to-styrene reaction, and it can be used in dehydrogenation and reforming reactions.

A methodology for selecting the new energy-efficient processes was developed. The selection criteria included operating conditions, energy requirement for reactions, ΔHE and equilibrium conversion based on Gibbs free energy, ΔGE; and thermodynamic feasibility of the reactions, catalyst conversion and selectivity, cost and life (time on stream to deactivation), and methods to regenerate catalysts. Also included were demand and potential sales of products and market penetration. In addition, cost of raw materials, energy, environmental, sustainable and other manufacturing costs were evaluated along with hydrogen consumption for hydrogenation reactions.

Based on the methodology for selecting new processes, twenty potential processes were identified as candidates for new energy efficient and environmentally acceptable plants. These processes were simulated using HYSYS, and a value added economic analysis was evaluated for each process. From these, fourteen of the most promising were integrated in the superstructure. These processes include production of methanol, ethanol, DME, propylene, formic acid, acetic acid, styrene, methylamines, graphite, and synthesis gas.

A base case of existing plants in a chemical production complex in the lower Mississippi river corridor was developed that included thirteen multiple plant production units plus associated utilities for power, steam and cooling water and facilities for waste treatment. The System was used with the base case and potentially new plants for carbon dioxide, and an optimal configuration of plants was determined for three different case studies.

In the first case, the System determined the optimum configuration of plants based on economic, environmental and sustainable costs. For this case, the profit of the optimal structure increased by 40%, environmental costs increased by 4.5%, and sustainable costs decreased by 17% compared to the base case. In the second study, the System determined the optimum configuration of plants for consuming all of the carbon dioxide from ammonia plant. In this case, the profit of the optimal structure increased by 24%, environmental costs decreased by 5.7%, and the sustainable costs increased by 5.5% when compared to the base case.

In the third study, the System determined the optimum configuration of plants for consuming all of the CO_2 available from ammonia plant operating at full production

capacity. In this case, the profit of the optimal structure increased by 21.7%, environmental costs increased by 10.2%, and the sustainable costs decreased by 33.3% when compared to the base case.

These results illustrated the capability of the Chemical Complex and Cogeneration Analysis System to select an optimum configuration of plants in a chemical production complex and incorporate economic, environmental and sustainable costs. These results are typical of what can be expected from applying the System to existing chemical production complexes worldwide. The Chemical Complex and Cogeneration Analysis System has been developed by industry-university collaboration, and the System is available from the LSU Minerals Processing Research Institute’s web site www.mpri.lsu.edu at no charge. Also, all of the HYSYS simulations given in this research and the Chemical Complex Analysis program and users manual are available in the CD included with this thesis.

CHAPTER ONE: INTRODUCTION

This chapter serves as an introduction to the growing concern over carbon management, concept of CO_2 conversion and utilization emphasizing the scope and potential for CO_2 reuse. This chapter also provides information about the various sources of carbon dioxide emissions, global climate change involved with these emissions, governmental regulations and ways to reduce these emissions. The relationship between sustainable development and Responsible Care will be discussed.

Many industrial manufacturing processes emit carbon dioxide to the atmosphere, for example from synthesis gas manufacture and combustion processes. The CO_2 thus vented is causing an increased concentration in the atmosphere and is contributing to greenhouse effect. Global warming is caused by this accelerative accumulation of CO_2 in the atmosphere. These emissions should be mitigated if the problem of global warming is to be controlled.

The objective of this research is to identify and design new industrial processes that use carbon dioxide as a raw material, and show how these processes can be integrated into existing chemical complexes. This will be done using Chemical Complex and Cogeneration Analysis System. This System is used to determine the optimal configuration of plants from a superstructure of possible plants. 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. The optimal configuration of plants in a chemical complex is obtained by solving the problem as a Mixed Integer Nonlinear Programming model (MINLP).

Incorporating the new designed processes that use carbon dioxide as a feedstock develops the superstructure. Economic, environmental, and sustainable costs are incorporated into the objective function of the chemical complex. Information about chemical complex optimization is presented next.

A) Overview of Chemical Production Complexes

The domestic chemical industry is an integral part of the nation's economy and has consistently contributed a positive balance of trade except for the last three years. 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.

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 (Hertwig et al., 2000). The focus of pollution prevention has transformed from being one of environmental issue to one of key business opportunity. This resulted in the increased business value of pollution prevention and industrial ecology (one company's wastes are raw materials for another company) (Hertwig et al., 2000). Emphasis on pollution prevention has broadened to include tools like total cost accounting (TCA), life cycle assessment (LCA), sustainable development and eco-efficiency. However, these tools have not developed as rapidly in the past two decades as has the opportunity to apply them (Hertwig et al., 2000).

Improvement of chemical processes can be very challenging and requires a balance of safety, reliability, economics, and quality. The environmental and societal impact of such processes should also be acceptable (Hertwig et al., 2000). Tools like total cost accounting (TCA), life cycle assessment (LCA), and sustainability metrics are creating a new view of plant design and product development. Modeling will play an important role in defining the best plants, products and operations, and optimization with multiple objective functions will incorporate economic and environmental effects (Hertwig et al., 2000). This trend in business value of pollution prevention will provide opportunities to use modeling technology to describe and predict the performance of new processes including environmental and sustainability evaluations (Hertwig et al., 2000). A brief overview of total cost accounting (TCA) is described below.

1) Total Cost Accounting

Total or full cost accounting identifies the real costs associated with a product or process. It organizes different levels of costs and includes direct, indirect, associated and societal costs (Hertwig et al., 2000). A detailed report on total cost accounting methodology has been developed by the Center for Waste Reduction Technology (CWRT) of the American Institute of Chemical Engineers (AIChE) (Constable, 1999). There are five types of costs used in the AIChE/CWRT TCA methodology. These are direct cost for the manufacturing site, potentially hidden corporate and manufacturing site overhead costs, future and contingent liability costs, internal intangible costs, and external costs (Hertwig et al., 2000).

The chemical complex and cogeneration analysis system described earlier determines the optimal configuration of chemical plants from a superstructure of possible plants. The objective function of the model incorporates the economic, environmental, and sustainable costs adapted from the TCA methodology.

B) Greenhouse Effect and Climate Change

The main constituents of greenhouse gases are CO_2, CH_4, N_2O, water vapor, chlorofluorocarbons, aerosols, etc. Carbon dioxide accounts for 83 percent of U.S. greenhouse gas emissions in 1998. These emissions show an increase of 0.3 percent than those emitted in 1997 (EIA, 1998b). The major constituents of greenhouse gases are shown in Figure 1.1. The numerical values in the Figure 1.1 indicate percentage U.S. greenhouse gas emissions in 2000.

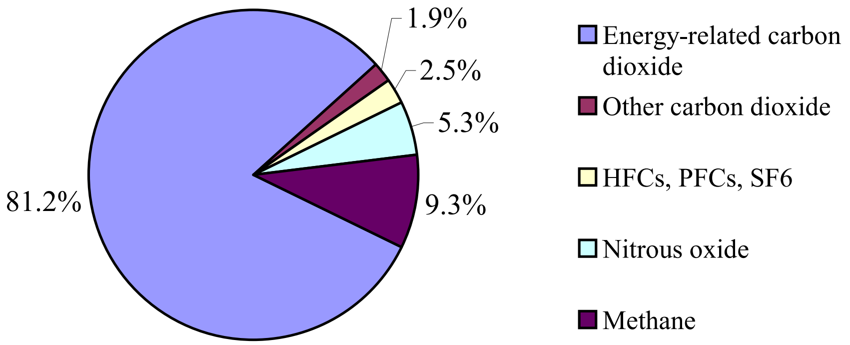


Figure 1.1 Greenhouse Gas Emissions by Gas in U.S.,2000, revised from EIA, 2001

These gases do not absorb solar radiation that reaches earth's surface and lower atmosphere. The incoming solar radiation falls in the visible and ultraviolet spectra (Halmann, 1999). The earth's surface absorbs this radiation and reflects heat in the form of infrared radiation. The greenhouse gases trap the outgoing infrared radiation in earth's lower atmosphere and prevent it from escaping into outer space. In this way, temperature is maintained on the earth's surface. The average surface temperature of earth is 15°C. If there were no greenhouse gases present, the surface temperature of the earth can be calculated to be -19°C (Halmann, 1999). This is a natural process and is called the natural greenhouse effect. Current life on earth could not be sustained without the presence of the natural greenhouse effect.

There has been 25% increase in the atmospheric concentrations of several greenhouse gases since large-scale industrialization began some 150 years ago (EIA, 1998a). The release of these greenhouse gases, which stays in the atmosphere for a long time, has intensified the natural greenhouse effect.

Assessing the available scientific, technical, and socio-economic information on the climate change indicated that the global mean surface air temperature has increased in the range approximately 0.3 to 0.6°C (0.5 to 1.1°F) since the late 19th century (EIA, 1998a). Additional climate models project that the global mean air surface temperatures may increase by 1.0 – 3.5°C between 1990 and 2010 (EIA, 1998a). The global mean temperature changes from 1880 to 2000 were shown in Figure 1.2 (EPA, Global Warming Website).

This increase in temperature may cause other detrimental changes in weather like the change in wind patterns, amount of precipitation, rise in the sea level threatening coastal communities, and may result in severity in floods and droughts (EIA, 1998a). Increase in temperature results in melting more ice and the snow covers in Northern Hemisphere, and floating ice in the Arctic Ocean has decreased. More melting resulted in the rise of 4 – 8 inch sea level rise globally over the past century (EPA, Global Warming Website). Evaporation will increase due to global warming which results in increase of precipitation globally. The global precipitation over land has increased by over 1% (EPA, Global Warming Website). EPA further projected that the soil moisture is likely to decline in many regions, and intense rainstorms are likely to become more frequent. This may cause an ecological change that could threaten agricultural productivity and survival of natural forests (EIA, 1998a). Thus climate change is more than just a global warming trend.

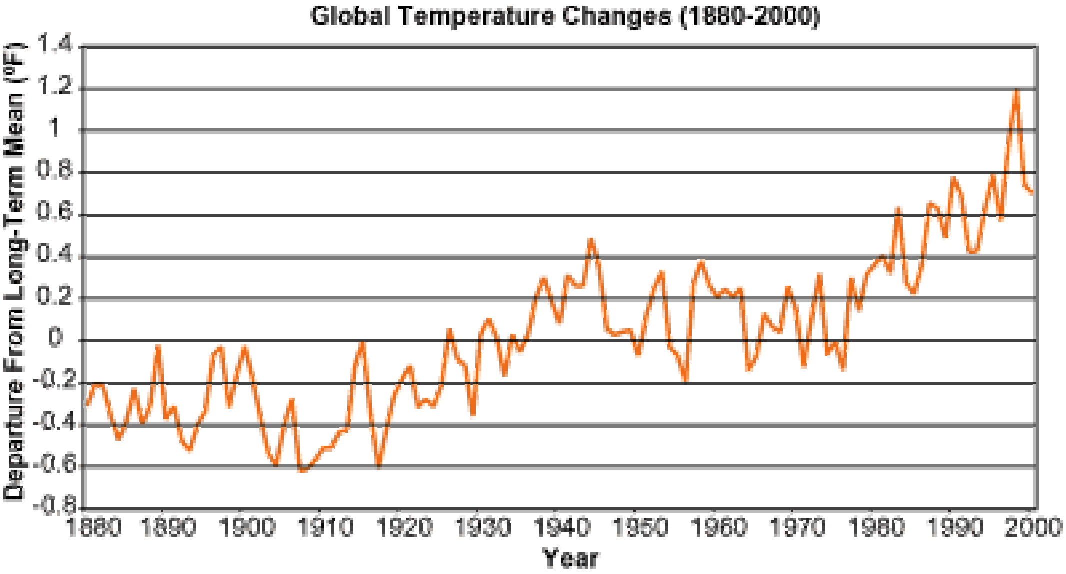


Figure 1.2. Global Mean Temperature Changes Over the Past Century
Source: (http://yosemite.epa.gov/oar/globalwarming.nsf/content/climate.html)

1) Estimation of Greenhouse Gas Emissions

Greenhouse emissions are measured by converting the gases into their carbon equivalent based on their global warming potentials (GWPs). GWP of a gas is defined as its total impact of adding a unit of greenhouse gas to the atmosphere during its lifetime. The atmospheric lifetime of a gas plays an important role in estimating its GWP. GWP value of a gas is reported relative to some reference gas, which is generally carbon dioxide. Thus GWP of carbon dioxide is taken as unity. GWP is calculated by multiplying instantaneous radiative forcing with concentration of the gas and integrating over its atmospheric lifetime. Using GWPs, the greenhouse gases are converted to their carbon dioxide equivalents and are further converted to their carbon equivalents by multiplying with 12/44, which is the ratio of molecular weights of carbon and carbon dioxide.

A list of various greenhouse gases is shown in Table 1.1 with their atmospheric concentrations and the rate of change of their concentration and their atmospheric lifetimes. The atmospheric concentration of carbon dioxide increased from 278 ppmv in pre-industrial times to 367 ppmv in 1999, a 31 percent increase in its atmospheric concentration (EPA, 2002). The global warming potential (GWP) values and the atmospheric lifetimes of various greenhouse gases are shown in Table 1.2. The GWP value of a gas is given by

$$\mathrm{GWP} = \frac{\int_0^T a_i c_i \, dt}{\int_0^T a_{CO_2} c_{CO_2} \, dt} \qquad \textbf{(1)}$$

where, a_i and a_{CO2} are the instantaneous radioactive forcing due to unit increase in concentration of species i and carbon dioxide respectively, c_i and c_{CO2} are the atmospheric concentrations of species i and carbon dioxide respectively, and T is the atmospheric lifetime.

The relationship between gigagrams (Gg) of a gas and Tg carbon dioxide equivalent is given by

$$\text{Tg CO}_2\text{ Eq.} = (Gg\ \ of\ \ gas)\ \text{x}\ (GWP)\ \text{x}\ \left(\frac{Tg}{1000Gg}\right) \qquad \textbf{(2)}$$

where, Tg CO_2 Eq. is teragrams of carbondioxide equivalents, and

Gg is Gigagrams (equivalent to thousand metric tons).

GWP = Global Warming Potential

Tg = Teragrams

Table 1.1 Global atmospheric concentration (ppm unless otherwise specified) and rate of concentration change (ppb/year) of selected greenhouse gases (EPA, 2002).

Atmospheric Variable	**CO_2**	**CH_4**	**N_2O**	**SF_6[a]**	**CF_4[b]**
Pre-industrial atmospheric concentration	278	0.700	0.270	0	40
Atmospheric concentration (1998)	365	1.745	0.314	4.2	80
Rate of concentration change [b]	1.5[c]	0.007[c]	0.0008	0.24	1.0

[a] Concentrations in parts per trillion (ppt) and rate of change in ppt/year.

[b] Rate is calculated over the period 1990 to 1999.

[c] Rate has fluctuated between 0.9 and 2.8 ppm per year for CO_2 and between 0 and 0.013 ppm per year for CH_4 over the period 1990 to 1999.

Table 1.2. Global Warming Potentials (GWP) and Atmospheric Lifetimes (Years) of various greenhouse gases (EPA, 2002).

Gas	**Atmospheric Lifetime**	**100-year GWP[a]**	**20-year GWP**	**500-year GWP**
Carbondioxide (CO_2)	50 - 200	1	1	1
Methane (CH_4)[b]	12 ± 3	21	56	6.5
Nitrous Oxide (N_2O)	120	310	280	170
HFC-23	264	11,700	9,100	9,800
HFC-125	32.6	2,800	4,600	920
HFC-134a	14.6	1,300	3,400	420
HFC-143a	48.3	3,800	5,000	1,400
HFC-152a	1.5	140	460	42
HFC-227ea	36.5	2,900	4,300	950
HFC-236fa	209	6,300	5,100	4,700
HFC-4310mee	17.1	1,300	3,000	400
CF_4	50,000	6,500	4,400	10,000
C_2F_6	10,000	9,200	6,200	14,000
C_4F_{10}	2,600	7,000	4,800	10,100
C_6F_{14}	3,200	7,400	5,000	10,700
SF_6	3,200	23,900	16,300	34,900

[a] GWPs above are calculated over 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 production of CO_2 is not included.

2) Greenhouse Gas Emissions

Greenhouse gases are 83% carbon dioxide (CO_2) as shown in Figure 1.1. The U.S. greenhouse gas emissions represented in million metric tons of carbon equivalents from 1990 to 2001 are shown in Table 1.3. The U.S. greenhouse gas emissions have increased at an average of 1.3 percent every year from 1990 to 2000 (EIA, 2000a). The emissions increased by 2.5 percent in 2000 over the previous year and then decreased by 1.2 percent in 2001 when compared to that in 2000 (EIA, 1990 - 2001). This decline is the largest percentage annual decline in total U.S. greenhouse gas emissions during 1990 to 2001 time period.

Table 1.3. U.S. Greenhouse gas emissions from 1990 – 2001. (EIA, 1998 - 2002).

Year	1990	1992	1994	1995	1996	1997	1998	1999	2000	2001
Carbon Equivalent (Million Metric Tons)	1633	1643	1702	1719	1767	1791	1803	1833	1906	1883

In summary, increased concentration of greenhouse gases in the atmosphere increases the greenhouse effect, and this in turn has an adverse effect on climatic changes. Greenhouse gas emissions are estimated based on global warming potential (GWP) of each gas.

C) Carbon Dioxide – A Greenhouse Gas

1) Sources of CO_2 Emissions

The sources of CO_2 emissions can be categorized into three divisions. They are stationary, mobile and natural sources (Song, 2002). A detailed list of stationary, mobile and natural sources for the CO_2 emissions is presented in Table 1.4. Stationary and mobile sources combined together account for the total CO_2 emissions from anthropogenic sources. The CO_2 emission from natural sources is a two-way flux exchange process between various interfaces of atmosphere, terrestrial biosphere, well-mixed layer of the ocean, and deep ocean that is an unmixed layer (Flannery, 2000).

Exchange of carbon dioxide flux between various interfaces along with CO_2 concentration in these interfaces is given in Figure 1.3. The largest flux exchange occurs between atmosphere and terrestrial biota, and between atmosphere and surface waters of ocean. In contrast to the above, CO_2 emissions from anthropogenic sources is a one-way flux exchange process.

Table 1.4. Sources of CO_2 Emissions. (Song, 2002)

Stationary Sources	**Mobile Sources**	**Natural Sources**
Fossil Fuel-based Electric Power Plants	Cars, and Sports Utility Vehicles	Humans
Independent Power Producers	Trucks and Buses	Animals
Manufacturing Plants in Industry	Aircrafts	Plant & Animal Decay
Commercial & Residential Buildings	Trains & Ships	Land Emission/Leakage
Flares of Gas at Fields	Construction Vehicles	Volcano
Military & Government Facilities	Military Vehicles & Devices	Earthquake

For the emissions from natural sources, there is essentially no opportunity for reduction of these emissions (Flannery, 2000). Carbon management is a potential solution for the reduction of anthropogenic sources. The United States accounts for 24% of global carbon dioxide emissions (Burtraw, 2001). Burning of fossil fuels is the main source of carbon dioxide emissions worldwide. Many countries are consuming fossil fuels in stationary and mobile devices and are thus contributing to these emissions. Carbon dioxide emissions from consumption and flaring of fossil fuels in 1999 in some selected countries are shown in Table 1.5. It is projected that the rate of these emissions tends to decrease in developed countries in future but they continue to increase in the developing nations (Flannery, 2000). United States is the nation with the largest carbon dioxide emissions in the world currently.

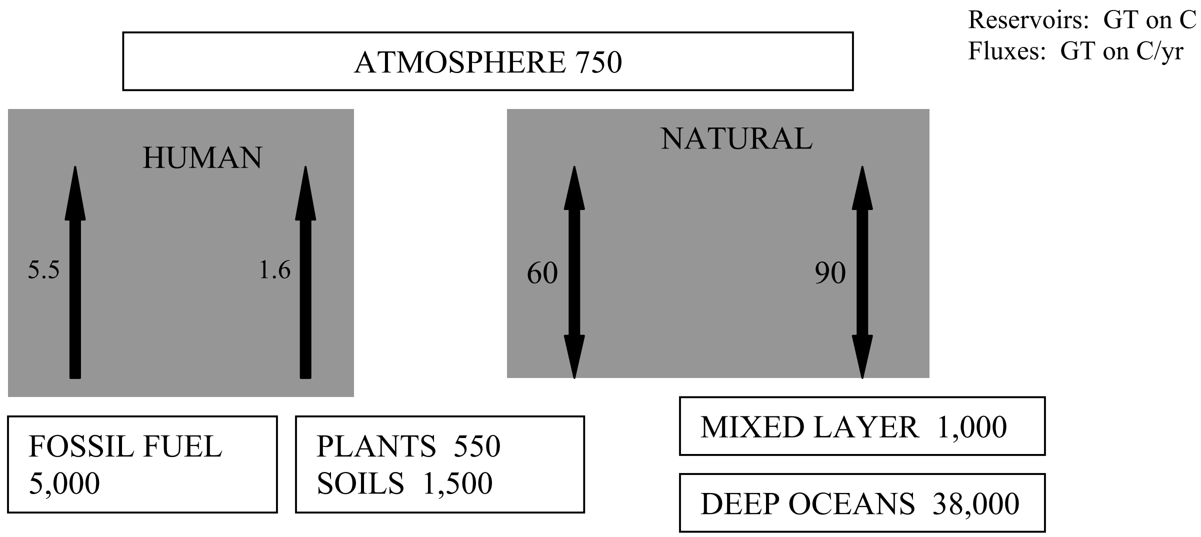


Figure 1.3 The Carbon Cycle, from IPCC (1995)

Table 1.5. World Carbon Dioxide Emissions from the Consumption and Flaring of Fossil Fuels in 1999 (Unit: Million Metric Tons Carbon Equivalent), from EIA, 2002.

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**

A more detailed list of U.S. CO_2 emissions and sinks between 1990 and 2000 from anthropogenic sources is presented in Table 1.6. As can be seen from Table 1.6, the main anthropogenic source is burning of fossil fuels.

Table 1.6. U.S. CO_2 Gas Emissions and Sinks from 1990 to 2000 (Tg CO_2 Eq) (EPA, 2002)

Gas/Source	**1990**	**1995**	**1998**	**2000**
CO_2	**4,998.5**	**5,305.9**	**5,575.1**	**5,840.0**
Fossil Fuel Combustion	4,779.8	5,085.0	5,356.2	5,623.3
Natural Gas Flaring	5.5	8.7	6.3	6.1
Cement Manufacture	33.3	36.8	39.2	41.1
Lime Manufacture	11.2	12.8	13.9	13.3
Limestone and Dolomite Use	5.2	7.0	8.2	9.2
Soda Ash Manufacture and Consumption	4.1	4.3	4.3	4.2

Table 1.6. (Continued)

Carbon dioxide Consumption	0.8	1.0	1.4	1.4
Waste Combustion	14.1	18.6	20.3	22.5
Titanium Dioxide Production	1.3	1.7	1.8	2.0
Aluminum Production	6.3	5.3	5.8	5.4
Iron and Steel Production	85.4	74.4	67.4	65.7
Ferroalloys	2.0	1.9	2.0	1.7
Indirect CO_2	30.9	29.5	28.2	26.3
Ammonia Manufacture	18.5	18.9	20.1	18.0
International Bunker Fuels [a]	113.9	101.0	112.9	100.2

[a] Emissions from International Bunker Fuels are not included in totals.

The U.S. CO_2 emissions from various sectors are presented in Table 1.7. The significant contribution from residential sector is because of the increase in demand for heating fuels related to abnormally cold weather. A 3.4 percent increase in the demand for these heating fuels was noticed in the year 2000 alone when compared with the 1995 level (EIA, 2000b). The two main sources of CO_2 emission within industrial sector are manufacturing processes of industrial products where CO_2 is obtained as a byproduct (such as manufacturing of cement, limestone, and hydrogen) and from energy supply by combustion of fossil fuels, which produces CO_2 (EIA, 2000b). This energy supplied may be either process heat or electricity.

Table 1.7. U.S. CO_2 emissions from different sectors (million metric tons of carbon equivalent) (Song, 2002).

CO_2 Emission Sources	**1980**	**1990**	**1997**
Residential Sector	248	253	286
Commercial Sector	178	207	237
Industrial Sector	485	454	483
Transportation Sector	378	432	473
Electric Utilities	418	477	523

The distribution of carbon dioxide emissions by selected manufacturing industries in 1998 in the U.S. is shown in Figure 1.4. The total emissions are 402.1 millions of metric tons carbon equivalent, and the petroleum and coal products industry and the chemical industry are 44% of the total, or 175 metric tons carbon equivalent per year in1998 (EIA, 2001).

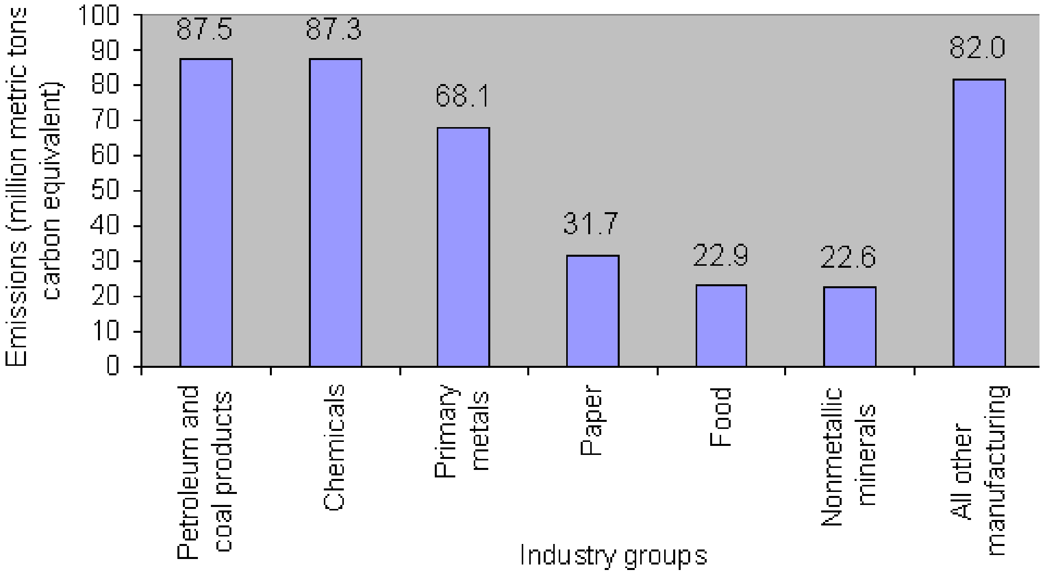


Figure 1.4 Total Energy-Related Carbon Dioxide Emissions for Selected Manufacturing Industries in 1998 (EIA, 2001).

In summary, the carbon dioxide emissions from anthropogenic sources should be mitigated. More effective conversion and utilization of carbon dioxide is a potential solution to reduce these emissions.

D) CO_2 Conversion and Utilization

CO_2 conversion and utilization should be an integral part of carbon management. As an example of utilization of CO_2, consider the synthesis of urea where CO_2 is used as a raw material. The chemical reaction involved in the urea synthesis is given below.

$$CO_2 + NH_3 \rightarrow H_2N\text{-}CO\text{-}NH_2 + H_2O \qquad \textbf{(3)}$$

Urea has the industrial applications as a fertilizer and as a monomer for thermosetting plastics.

Approximately, 110 million metric tons per year of carbon dioxide are used as a raw material for the production of urea, methanol, polycarbonates, cyclic carbonates and speciality chemicals (Arakawa, et al., 2001). The largest use is for urea production that reached about 90 million metric tons per year in 1997 (Creutz and Fujita, 2000). However, 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). Ammonia production consumes hydrogen that is obtained from synthesis gas after removing carbon dioxide. However, about 6.8 million tons per year of carbon dioxide are available from ammonia plants in the U.S., and urea and methanol plants only consume 4.0 million tons per year (Wells, 1999). This leaves an excess of 2.8 million metric tons per year of high purity carbon dioxide that is discharged into the atmosphere in the U.S. Also, there is approximately another 19 million metric tons of relative high purity carbon dioxide vented from refineries and other chemical plants in the U.S. that use hydrogen from synthesis gas.

The chemical industry has pledged an industry wide goal of reducing its greenhouse gas intensity (ratio of net greenhouse gas emissions to production) by 18% to 1990 levels by 2012 through the American Chemistry Council (Chemical Engineering, 2003). Also, the DOE Energy Information Administration (EIA) recently issued a report on Voluntary Reporting of Greenhouse Gases in 2001 describing 228 U. S. companies that had performed 1,705 projects to reduce or sequester greenhouse gases (EIA, 2003). A detailed breakdown, and a total of 68 million metric tons for carbon equivalent was reduced in 2001 of which 50 million metric tons were from direct reduction, 16 million metric tons from indirect reduction and 2 million tons were sequestered. The electric power industry was the main contributor with 41 million metric tons per year from direct reduction and 5.0 million metric tons per year from indirect reduction using reduced carbon content in fuel, and in increased efficiency in generation, transmission and distribution. Beyond the power industry, essentially all major manufacturing companies were included. This report states that these reductions were significant considering total U. S. emissions were 1,627 metric tons of carbon equivalent per year.

A summary of carbon dioxide emissions worldwide, by nations, by the U.S. by U.S. industry and the chemicals, coal and refining industries is given in Table 1.8. The emissions of carbon dioxide were discussed in detail in the earlier section. However, this table provides as a summary of most of the information discussed. In the lower Mississippi River corridor agricultural chemical complex there are 0.183 million metric tons carbon equivalent high purity excess CO_2 per year (Hertwig et al., 2002).

Table 1.8. CO_2 Emissions and Utilization (Million Metric Tons Carbon Equivalent/Year)

CO_2 emissions and utilization	**Reference**
Total CO_2 added to the atmosphere Burning fossil fuels 5,500 Deforestation 1,600	IPCC (1995)
Total worldwide CO_2 from consumption and flaring of fossil fuels United States 1,526 China 792 Russia 440 Japan 307 All Others 3,258 World Total 6,322	EIA (2002)
U.S. CO_2 emissions Industry 630 Buildings 524 Transportation 473 Total 1,627	Stringer (2001)
U.S. industry (manufacturing) Petroleum, coal products and chemicals 175	EIA (2001)
Chemical and refinery (BP) Combustion for energy requirements and flaring 97% Noncombustion direct CO_2 emission 3%	McMahon (1999)
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)

1) Potential for CO_2 Utilization

A potential upper limit of carbon dioxide use as a raw material has been estimated by Song, 2002. This 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. This tonnage is comparable to carbon dioxide emissions from all U.S. fossil fuel power plants.

2) Challenges for CO_2 Utilization

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).

In Figure 1.5, the total U.S. carbon emissions are shown from 1990 to 1999 and also the projected emissions to 2020. The total carbon emissions in 1990 were about 1.4 GtC per year. The black squares from the year 1990 to 1999 shows the actual emissions. There is a decline in the emissions in 1991 because of economic recession. This economic recession produced a small decline of about ten million metric tons per year in net emissions.

Based on Figure 1.5, the total emissions in 2010 will be 44% above the Kyoto target, and these emissions will be 62% above the target in 2020. The insert in Figure 1.5 shows the break down of the 1997 emissions into three classes – electric power use or the utilities, transportation, and all other uses combined. From Table 1.7 discussed earlier, the emission from electric utilities and transportation in the year 1997 were 523 and 473 million metric tons of carbon equivalent. The author did not specify the sectors that were considered for the third class in the insert. These three classes combined together add up for the total emissions in 1997.

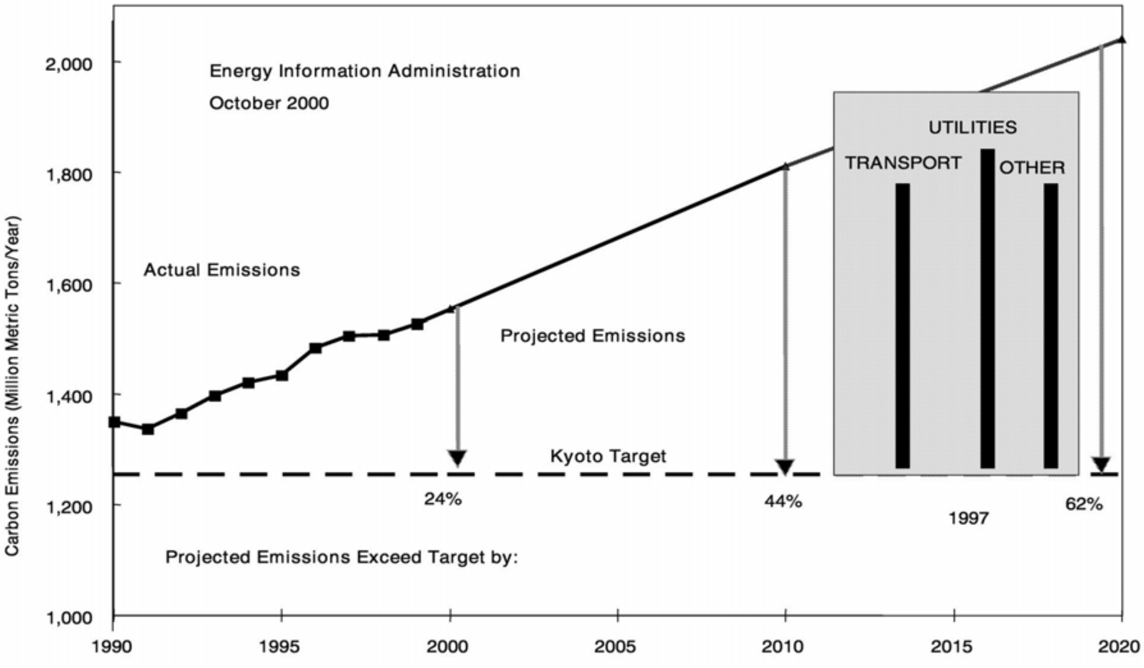


Figure 1.5 U.S. Carbon Emissions: Projected Versus the Kyoto Target.
Source: Flannery, 2000.

The total carbon dioxide emission in U.S. in the year 1997 was 1500 million metric tons of carbon equivalents (EIA, 1997). Thus, these emissions were high enough that even eliminating one of the above classes will still put the net emissions well above the Kyoto target. Thus, the need for the introduction of the new technology and the change of infrastructure are desired (Flannery, 2000). The rate at which these new technologies would be developed is also an equally important issue compared to the development of these technologies. The important issue would be how to introduce new technology in a small scale and then get them to grow into widespread commercial use (Flannery, 2000).

No single new technology will solve the entire problem. There should be an emergence of a number of promising new technologies that could contribute to the carbon dioxide emission reductions (Flannery, 2000). All of them have to overcome challenges of economics, performance, and associated environmental impacts. Performance, cost, safety, regulatory compliance, and low environmental impacts are some of the barriers identified to be able to make a new technology into widespread commercial use (Flannery, 2000). For example, consider the case of separation and sequestration of carbon dioxide from large combustion facilities. Among the critical design considerations is whether to combust in air or in oxygen. In either case, procedures must be designed to remove oxygen from air or to remove carbon dioxide from flue gas. Additional procedures are needed to compress the carbon dioxide to high pressure in order to move it elsewhere and dispose of it for long periods of time (Flannery, 2000).

Introduction of new technology solutions require extensive research and development to identify the current barriers, as well as finding solutions that improve performance, cost, safety, environmental acceptability, and consumer acceptability (Flannery, 2000).

3) Research Strategies for CO_2 Utilization

Carbon dioxide can be used as a reactant or co-feed in various non-catalytic chemical processes and heterogeneous or homogeneous catalytic processes. It can also be used in other reactions like photochemical, photo-catalytic reduction, bio-chemical, and electrocatalytic conversion. Most of the processes are subjects of research in the laboratory, and few processes have reached large-scale production (Song, 2002). Figure 1.6 is a convenient way to show the range of reactions for carbon dioxide. It can be used as the whole molecule in reactions, and it can be used as a carbon source or as an oxygen source (Creutz and Fujita, 2000).

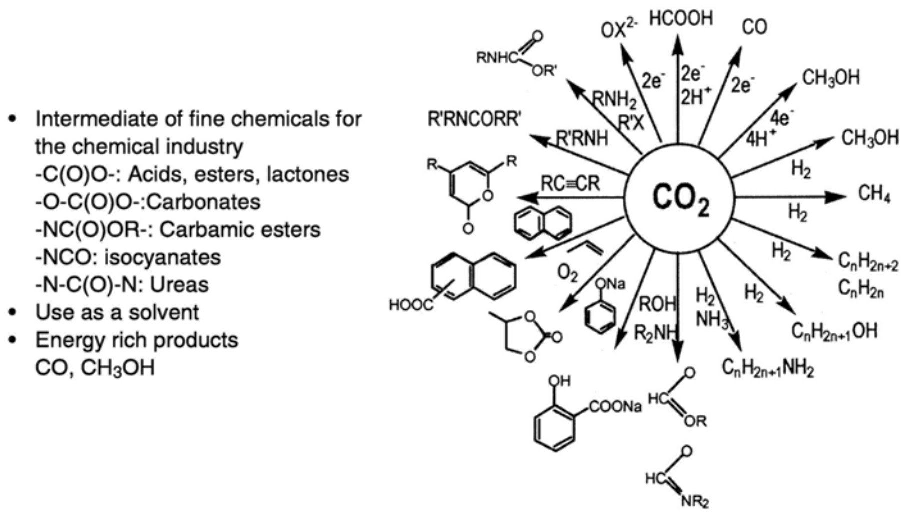


Figure 1.6 Utilization of CO_2 in Synthetic Chemistry.
Source: Creutz and Fujita, 2000

The synthesis of urea from ammonia and carbon dioxide, and the production of salicylic acid from phenol and carbon dioxide are good examples of the large-scale production processes where carbon dioxide is utilized as a raw material. The following are some of the possible ways to expand the utilization of carbon dioxide in chemical industry.

a) Developing New Alternate Processes

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 (Song, 2002). Production of methanol and synthesis of hydrocarbon chemicals using CO_2-rich synthesis gas instead of using H_2/CO rich synthesis gas as a raw material is a good example (Song, 2002). There is a need for more research towards developing new alternate processes for using carbon dioxide.

For example, it was shown that a 100 million pound per year acetic acid plant using a new catalytic process for the direct conversion of carbon dioxide and methane to acetic acid had a potential energy savings 275 billion BTUs per year compared to a conventional plant (Hertwig, et al., 2002). Also, there would be a reduction in NO_x emissions of 3.5 tons per year base on steam and power generation by cogeneration. In addition, the carbon dioxide reduction from reduced steam requirements would be 12,600 tons per year, and the total carbon dioxide reduction would be 49,100 tons per year from converting it to a useful product (36,700 tons per year) and reduced energy generation (Hertwig, et al., 2002). More details about this potentially new process will be discussed in Chapter Two.

b) Increasing the Commercial Applications of Products from CO_2

The scope and potential for the utilization of CO_2 for chemicals and materials is limited. Expanding the market for these chemicals and materials might be one of the effective solutions for CO_2 utilization (Song, 2002). If the commercial applications of the products produced from CO_2 were increased, then the demand for these products increases which in turn increases demand for its raw material CO_2. In this way, more CO_2 can be utilized and also the chemical market potential would expand. For example, one of the main areas of CO_2 utilization in present chemical industry is the manufacture of urea. If the application of urea-based polymers were expanded, then this would increase the demand for urea synthesis. Thus the demand for its raw material CO_2 would also increase prompting an increase in CO_2 utilization (Song, 2002).

c) Effective CO_2 Sequestration

The annual production of U.S. synthetic plastics is about 36.7 million metric tons in 1999 (Song, 2002). The applications of plastics are also increasing every year. These plastics after being used will eventually get sequestered in a landfill at the end of their useful life. By converting carbon dioxide to plastics, the chemical industry is making profit and at the same time is contributing to sequestration of carbon dioxide. This is a more effective way of CO_2 sequestration instead of directly sequestering carbon dioxide because of the capital investments associated with the direct sequestration. Thus the increase in the market for synthetic plastics is desired in this perspective.

The costs for sequestering carbon dioxide in geological formations, oceans and natural systems have been summarized by Kim and Edmonds, 2000. They estimated the cost to range from \$120 to \$340 per metric ton of carbon equivalent. Also, they estimated that this cost would drop to \$50 per ton of carbon equivalent by 2015.

d) Replacement of Hazardous Substances

In some processes where the raw material or the reactant is hazardous or not an environmentally benign chemical, then replacing this substance with carbon dioxide, as a reactant following a new reaction pathway may be possible. Replacement of phosgene with carbon dioxide in the production of dimethyl carbonate is a good example in this category (Song, 2002).

Exposure to phosgene results in severe respiratory effects, including pulmonary edema and pulmonary emphysema (EPA, Air Toxics Website). Thus, phosgene is considered as a hazardous chemical. Using carbon dioxide as a co-feed in such processes has two-way advantages – getting rid of hazardous chemicals, and also increasing the utilization of carbon dioxide.

Dimethyl carbonate ($CH_3OCOOCH_3$) is produced industrially from carbon monoxide with phosgene as an intermediate, reaction 4, and two other processes where carbon monoxide is used directly, reactions 5 and 6 (Song, 2002). Both the chemicals carbon monoxide and phosgene are toxic in nature. Replacing these processes with new alternate routes using carbon dioxide as a raw material is shown in reaction 7.

Conventional Route (By SNPE Chemicals, 1970's):

$$CO + Cl_2 \rightarrow COCl_2 \text{ (Phosgene)}$$

$$COCl_2 + 2\,CH_3OH \rightarrow CH_3OCOOCH_3 + 2\,HCl \qquad \textbf{(4)}$$

EniChem DMC Process (By EniChem – 12000 tons/Yr)

$$CO + \tfrac{1}{2}\,O_2 + 2\,CH_3OH \rightarrow CH_3OCOOCH_3 + H_2O \qquad \textbf{(5)}$$

Ube DMC Process (By Ube Chemical – 3000 tons/Yr)

$$CO + 2\,CH_3ONO \rightarrow CH_3OCOOCH_3 + 2\,NO \qquad \textbf{(6)}$$

New CO_2-Based Route

$$CO_2 + 2\,CH_3OH \rightarrow CH_3OCOOCH_3 + H_2O \qquad \textbf{(7)}$$

e) Other Areas of CO_2 Utilization

The other areas for utilization of carbon dioxide are using CO_2 as a solvent for separation, as a medium for chemical reaction based on its physical and chemical properties (Song, 2002). Carbon dioxide can also be used in enhanced recovery of oil and natural gas, enhanced coal bed methane recovery where the requirement for purity of carbon dioxide is minimum; and thus, processing costs for separation and purification would be low (Song, 2002).

A brief review of chemical complexes in the world is presented in the next section. In particular, the chemical complex in the lower Mississippi River corridor is described, and the idea of applying Chemical Complex and Cogeneration Analysis System to these complexes is introduced below.

E) Chemical Complexes Around the World

The chemical production complex present in the lower Mississippi River corridor is shown in Figure 1.7. There are about 150 chemical plants that consume 1.0 quad (10^{15} BTUs per year) of energy and generate about 215 million pounds per year of pollutants

(Peterson, 1999). There is a carbon dioxide pipeline that connects several plants. Currently, there is approximately an excess 1.0 million metric tons per year of high purity carbon dioxide from ammonia production plant that is being vented to the atmosphere. The cost of carbon dioxide as a raw material is essentially the pumping cost of about \$2-3 per ton.

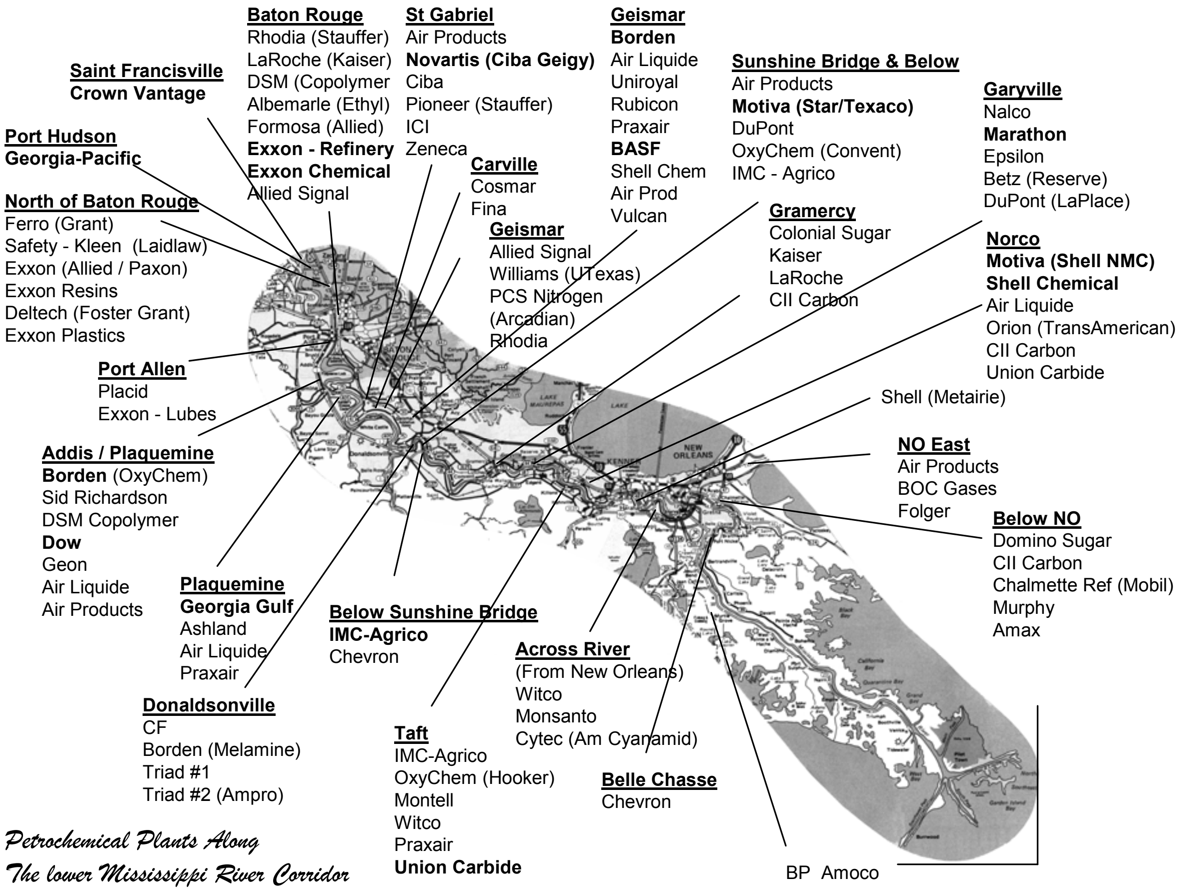


Figure 1.7 Plants in the Lower Mississippi River Corridor from Peterson, 1999.

The chemical production complex in lower Mississippi River corridor is one of several worldwide chemical complexes that can benefit from using carbon dioxide as a raw material and from the resulting reduced energy consumption. The various chemical complexes existing worldwide were given in Table 1.9. The results of this research and development will be applicable to these multi-plant complexes, especially the one in Houston, the largest complex in the world.

Table 1.9. Major Chemical Complexes around the world.

Continent	Name and Site	Notes
North America	• Gulf coast petrochemical complex in Houston area (U.S.A.) • Chemical complex in the Lower Mississippi River Corridor (U.S.A.)	• Largest petrochemical complex in the world, supplying nearly two-thirds of the nation's petrochemical needs
South America	• Petrochemical district of Camacari-Bahia (Brazil) • Petrochemical complex in Bahia Blanca (Argentina)	• Largest petrochemical complex in the southern hemisphere
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

F) Sustainable Development

Sustainable development is the concept of achieving the present needs without sacrificing the ability of the future to achieve its needs (Hertwig et al., 2000). A more recent definition proposed by Rittenhouse (2003) is "ensuring a better quality of life for everyone now and for generations to come". According to Terry F. Yosie, vice president for Responsible Care for American Chemistry Council, "sustainable development is still a concept where we need to learn a great deal from each other, one which is ideally suited toward working in partnership with other people. Sustainable development is a way to help companies become global and more competitive" (Watkins, 2002).

There has been a growing attention towards sustainable development in the recent past. Two summits were held exclusively for sustainable development in the past ten years. The Earth Summit in Rio de Janeiro in 1992 lifted environmental issues to a higher level of consideration in the global psyche (Rittenhouse, 2003). At this meeting, the UN proclaimed sustainable development to be the central organizing principle for worldwide economic development (Watkins, 2002). The World Summit for Sustainable Development (WSSD) was held September 2-11, 2002 in Johannesburg, South Africa. The main objective of the summit was the formal negotiations among the participating governments (Rittenhouse, 2003).

Sustainable development is focused on environmental, social, and economic areas. These three areas are often referred to as the "triple bottom line" (Rittenhouse, 2003). The environmental factors include climate change, ecosystem destruction, depletion of natural resources, and pollution of land, air, and water. The social factors consider human and worker's rights, the increasing poverty gap, governance, and ethics.

The economic factors include shareholder value and building capacity for development (Rittenhouse, 2003). The successful companies need to understand and perform in all three areas.

The challenge in sustainable development is to do the right thing in a way that makes business sense (Watkins, 2002). There are other important business-value reasons for the companies to address sustainable development (Rittenhouse, 2003). It protects and enhances their reputation, improves employee morale, increases productivity and reduces costs, strengthens customer relationships, and enhances business growth (Rittenhouse, 2003).

One important method used for measuring sustainability is the Sustainable Process Index (SPI). SPI is an ecological evaluation system specially developed for the requirements of process engineering (Narodoslawsky, 2001). The SPI was specially developed as a means to evaluate the viability of processes under sustainable economic conditions. It is based on mass and energy balances of the processes to be evaluated (Narodoslawsky, 2001).

1) Achieving Sustainable Development

According to Rittenhouse's report (2003), socially responsible investing (SRI) is an important business link for achieving sustainable development. This community invests in companies that are more responsible in environmental and social performance than their competitors (Rittenhouse, 2003). Such companies will have the potential to provide the best overall return. SRI is still a small part of the overall investment market, but it is growing, a good performance in this area can provide a possibility for a new set of shareholder (Rittenhouse, 2003). Social and environmental performances are becoming more important, not just as a right to operate, but also as a source of competitive advantage.

Global Environmental Management Initiative (GEMI) is a non-profit organization, which helps companies in focusing on the actions that bring most benefit along with sustainable development (Rittenhouse, 2003). Its recently published "Exploring Pathways to a Sustainable Enterprise: SD Planner" is a detailed and comprehensive self-assessment tool designed to help companies evaluate, plan for, and integrate sustainable development into business processes.

Emission trading is one possible way of meeting the sustainable development and reducing the greenhouse gas concentration. Emission-trading system for greenhouse gases is an important way to achieve sustainability according to Kyoto Protocol (EPA, 1999). Burtraw, 2001, mentioned the different approaches of carbon emission trading. One way to allocate the emission allowances is through a revenue-rising "auction". A second approach is grandfathering, patterned after the SO_2 trading program, in which allowances would be distributed on the basis of historic generation. A third approach is a generation performance standard (GPS) in which allowances would be allocated based on the shares of current electricity generation. The auction approach is more cost-effective than the other approaches – roughly 50% cheaper than grandfathering or the GPS (Burtraw, 2001).

The increase in the amount of greenhouse gases in the atmosphere has an adverse effect on achieving sustainability. Many companies are working together for the reduction of these greenhouse gases. The specific targets of some of the leading companies in USA on the reduction of these gases are given in Table 1.10.

Table 1.10. Greenhouse gas emissions reduction targets of some U.S. companies (C & EN, November 12, 2001, Page 21)

Company	**Greenhouse gas emission reduction target**	**Period**
Chemical/Petroleum		
Alcoa	25%	1990 - 2010
BP	10%	1990 - 2010
DuPont	65%	1990 - 2010
Shell	10%	1990 - 2002

Kyoto Protocol is one important protocol, which commits 38 industrialized countries to cut their greenhouse gas emissions between 2008 and 2012 to levels below the 1990 levels. 180 countries at Kyoto, Japan signed the Kyoto Protocol document, in December 1997. The emission targets vary for different countries among the developed and developing nations. For example, the targets were 8 percent below 1990 emissions for the European Union, 7 percent for the United States, and 6 percent for Japan (EPA, 1999). The protocol makes a down payment for meaningful participation of developing countries, but more has to be done in this area (EPA, 1999).

2) Sustainable Development and Responsible Care

Watkins (2002) in his report described the relationship between sustainable development and Responsible Care program. Responsible care is not the same as sustainable development. “Sustainable development is much bigger, tougher, and more diffuse than Responsible Care”, says Dawn Rittenhouse, director of Sustainable Development for the Dupont Co (Rittenhouse, 2003). Responsible Care is a defined set of codes and standards, summarized in six codes of management practice for the chemical industry to follow. Sustainable development, on the other hand, is not defined, and there are no documents to compare it to Responsible Care (Watkins, 2002). Part of the reason for the chemical industry’s progress has been the Responsible Care program. The chemical industry's commitment to Responsible Care has paved the way for progress on sustainability (Watkins, 2002). Thus, sustainable development can be achieved through Responsible Care.

Responsible Care and sustainable development has an intermeshing relationship with some common goals (Watkins, 2002). Loather Meinzer, head of the sustainability center at BASF says, "Responsible Care is an integral part of sustainable development".

Responsible Care program was formed with six codes of management practice in the early 1980s. Recent events like the terrorist attacks of September 11, 2001 in U.S., and the explosion ten days later at the Grande Paroisse fertilizer plant in Toulouse, France have brought safety and security issues into the limelight for all chemical companies (Watkins, 2002). Responsible Care has undergone a change in the light of these recent events. A seventh Responsible Care code dealing with security is being established (Watkins, 2002).

Chemical Manufacturer's Association (CMA) have developed "Responsible Care", also as a means of trying to change the public's perception of the chemical industry from one of ruthless, uncaring ambition, to one of trust, honesty and credibility (Hook, 1996). Events like the terrorist attacks in U.S. or the explosion in Toulouse illustrate the importance of ties between a plant and its community (Watkins, 2002). The most effective way to reassure the communities is to have an open dialogue with the community according to Michael Kern, senior vice president for environmental health and safety at Huntsman Corporation (Watkins, 2002). The most revolutionary aspect of Responsible Care program has been the establishment of community outreach programs, especially the convening of community advisory panels (CAPs). CAPs have contributed substantially to increased understanding of environmental issues faced by both industry and community (Hook, 1996).

G) Summary

The focus of business has changed from a regional basis to global basis and pollution prevention has become a major business opportunity (Hertwig et al., 2000). This trend has resulted in the improvement of tools like total cost accounting (TCA), life cycle assessment (LCA), and sustainable development (Hertwig et al., 2000). The Chemical Complex and Cogeneration Analysis System has been developed to determine the optimal configuration of the chemical plants and the objective function includes economic, environmental and sustainable costs using TCA methodology.

The increase in the concentration of greenhouse gases in atmosphere is causing an adverse effect in achieving sustainable development. The greenhouse gases emissions should be mitigated. Carbon dioxide is the dominant gas among the greenhouse gases, and it accounted for 83 percent of U.S. greenhouse gas emissions in 1998 (EIA, 1998). The United States accounts for 24 percent of total carbon dioxide emissions worldwide (Burtraw, 2001). The increase in carbon dioxide emissions is mainly due to anthropogenic sources and especially burning of fossil fuels. Effective conversion and utilization of carbon dioxide is a potential solution to mitigate greenhouse gas emissions.

Approximately, 110 million metric tons per year of carbon dioxide are used as a raw material for the production of urea, methanol, polycarbonates, cyclic carbonates and speciality chemicals (Arakawa, et al., 2001). Developing new alternate processes that use CO_2 and increasing the commercial applications of products produced from CO_2 are possible ways of mitigating carbon dioxide emissions (Song, 2002).

The chemical complex present in lower Mississippi River corridor contains about 150 plants that consume 1.0 quad (10^{15} Btu/yr) of energy and generate about 215 million pounds per year of pollutants (Peterson, 1999). Approximately an excess 1.0 million metric tons per year of high purity carbon dioxide from ammonia production that is being vented to the atmosphere.

Sustainable development is the concept that development should meet the needs of the present without sacrificing the ability of the future to meet its needs (Hertwig et al., 2000). Socially responsible investing (SRI) and global emissions trading are two important ways of achieving sustainable development (Rittenhouse, 2003 and EPA, 1999). Responsible Care is an integral part of sustainable development.

The chemical complex and cogeneration analysis system can be applied to any chemical complex worldwide to determine the optimal configuration of chemical plants. The next chapter describes the literature review of various processes that use carbon dioxide as a raw material. The structure of chemical complex and cogeneration analysis system will also be discussed.

CHAPTER TWO: LITERATURE REVIEW

The growing concern over the industrial emissions of greenhouse gases with an emphasis on carbon dioxide emissions was discussed in Chapter One. In Chapter Two, the various reactions where carbon dioxide can be used as a raw material will be reviewed. The literature review of various laboratory scale processes that use carbon dioxide as a raw material to produce other products will be briefly presented. These experimental studies will be discussed in more detail in the subsequent chapters. Also, the structure of Chemical Complex and Cogeneration Analysis System will be discussed.

A) Carbon Dioxide as a Raw Material

There has been an increased attention for the use of carbon dioxide as a raw material over the past two decades. There have been five international conferences and numerous articles in the past twenty years on carbon dioxide reactions that consider using it as a raw material (Song, et al., 2002, Creutz and Fujita, 2000, Steinberg, et al., 1999, Inui, et al., 1998, Sullivan, 1993, and Inoue and Yamazaki, 1982).

Increased utilization of carbon dioxide is desirable as it is an inexpensive and nontoxic starting material (Creutz and Fujita, 2000). In view of the vastness of its supply, carbon dioxide represents a possible potential source for C_1 feedstocks for the manufacture of chemicals and fuels, alternative to the current predominant use of petroleum-derived sources (Keene, 1993). An overview of the properties and reactivity of carbon dioxide is presented in the subsequent sections of this chapter.

B) Properties of Carbon Dioxide

The structure of a carbon dioxide molecule is linear. It is a thermodynamically stable molecule with bond strength measured at D = 532 kJ/mol

(Keene, 1993). Song, 2002 summarized the various physical and chemical properties of carbon dioxide and are presented in Table 2.1. The heat of formation (ΔH°) and Gibbs free energy of formation (ΔG°) of carbon dioxide are the two important properties in Table 2.1. These values were extensively used in this research to calculate the standard heat of formation and Gibbs free energy of the various CO_2 reactions, which are described in this chapter. The ΔH° and ΔG° values are the most important criterion for estimating the thermodynamic feasibility of a reaction. The significance of the heat of formation and Gibbs free energy of a reaction are discussed in Chapter Three.

Table 2.1. Physical and Chemical Properties of Carbon Dioxide (Song, 2002).

Property	**Value and Unit**
Heat of formation at 25°C	-393.5 kJ/mol
Entropy of formation at 25°C	213.6 J/K.mol
Gibbs free energy of formation at 25°C	-394.3 kJ/mol
Sublimation point at 1 atm	-78.5°C
Triple point at 5.1 atm	-56.5°C
Critical temperature	31.04°C
Critical pressure	72.85 atm
Critical density	0.468 g/cm^3
Gas density at 0°C and 1atm	1.976 g/L
Liquid density at 0°C and 1 atm	928 g/L
Solid density	1560 g/L
Specific volume at 1atm and 21°C	0.546 m^3/kg
Latent heat of vaporization At the triple point (-78.5°C) At 0°C	 353.4 J/g 231.3 J/g
Viscosity at 25°C and 1atm	0.015 cp
Solubility in water At 0°C and 1 atm At 25°C and 1 atm	 0.3346 g CO_2/100 g-H_2O 0.1449 g CO_2/ 100 g-H_2O

C) Reactivity of Carbon Dioxide

The reactivity of carbon dioxide and the potential means of promotion of its reactivity are described in this section. Some reactivity might be anticipated for carbon dioxide despite its linear symmetry and overall nonpolar nature of the molecule. This is because of the presence of π-electron density of the double bonds and the lone pairs of electrons on the oxygen atoms, or the electrophilic carbon atom (Keene, 1993). Reactions of carbon dioxide are dominated by nucleophilic attacks at the carbon, which result in bending of the O-C-O angle to about 120° (Creutz and Fujita, 2000).

Since CO_2 is a very stable molecule, consequently, energy must generally be supplied to drive the desired transformation. The reactions of carbon dioxide often require high temperatures, active catalysts, electricity or the energy from photons (Creutz and Fujita, 2000). Thus, generally the reactions involving carbon dioxide are endothermic, and they consume energy. For example, consider the reactions for steam reforming of methane and CO_2 reforming of methane. The CO_2 reforming requires about 20% more energy input when compared to steam reforming (Song, 2002). Both the reactions are useful for industrial applications as they give synthesis gas products with different H_2/CO molar ratios.

It is more energy demanding if carbon dioxide is used as a single reactant. However, since its Gibbs free energy is –394.4 kJ/mol, it becomes thermodynamically more feasible if carbon dioxide is used as a co-reactant with another reactant that has higher Gibbs free energy (Song, 2002). Methane, carbon (graphite), and hydrogen are some examples of co-reactants that have higher (less negative) Gibbs energy. As an example, consider the dissociation of carbon dioxide to carbon monoxide where CO_2 is used as a single reactant and reduction of CO_2 by H_2 where CO_2 is used as a co-reactant. The heat of reaction is less in the case where carbon dioxide is used as a co-reactant (Song, 2002).

$$CO_2 \rightarrow CO + \tfrac{1}{2} O_2 \qquad \Delta H° = +293 \text{ kJ/mol}, \Delta G° = +257 \text{ kJ/mol}$$
$$CO_2 + H_2 \rightarrow CO\ (g) + H_2O\ (g) \qquad \Delta H° = +51 \text{ kJ/mol}, \Delta G° = +28 \text{ kJ/mol}$$

D) Current Uses of Carbon Dioxide

The current largest use of CO_2 is in the synthesis of urea, a widely used fertilizer. About 110 megatons of CO_2 are used annually for the chemical synthesis (Arakawa, 2001). Of these, about 90 megatons were used for the production of urea in 1997 (Cruetz and Fujita, 2000). The reaction involved for the production of urea is given below.

$$CO_2 + NH_3 \rightarrow H_2N\text{-}CO\text{-}NH_2 + H_2O$$

Carbon dioxide is also used to produce salicylic acid, which is found in pharmaceuticals and cyclic organic carbonates (Cruetz and Fujita, 2000). Salicylic acid is produced by the reaction of sodium phenolate with CO_2 to produce sodium salicylate. The formed sodium salicylate is converted to salicylic acid by the addition of sulfuric acid. Sodium sulfate is obtained as a by-product. Aspirin is produced from salicylic acid. The reaction path involved in the production of salicylic acid and aspirin is shown below.

$$CO_2 + C_6H_5ONa \rightarrow C_6H_5(COONa)OH$$

$$\xrightarrow{H^+} C_6H_5(COOH)OH \quad \text{salicylic acid}$$

$$\xrightarrow{(CH_3CO)_2O} C_6H_5(COOCH_3)COOH$$

aspirin

Methanol for chemical and fuel use is produced by reacting carbon dioxide and hydrogen catalytically. Methanol can also be dehydrated to form gasoline-like fuels (Steinberg, et al., 1999). The reaction involved in the production of methanol from CO_2 and H_2 is given below.

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

Carbon dioxide is also used in enhanced oil recovery operations. The amount of CO_2 used annually in U.S. for enhanced oil recovery was estimated to be 1.14×10^9 tons per year (Steinberg, et al., 1999). Carbamates used in inorganic chemical production are also produced from carbon dioxide by reacting with amines and salt. The reaction involved is shown below.

$$CO_2 + 2CH_3NH_2 + NaCl \rightarrow CH_3NH_2COONa + CH_3NH_2Cl$$

Other uses include the utilization of carbon dioxide in refrigeration systems, carbonated beverages, fire extinguishers, inert gas-purging systems, blasting systems for mining coal, and secondary sewage sludge treatment. Supercritical carbon dioxide is used as a solvent for promoting difficult chemical reactions (Steinberg, et al., 1999).

E) Reactions of Carbon Dioxide

In Table 2.2, various reactions where CO_2 is used in the organic chemical synthesis are listed. The reactions in Table 2.2 include hydrogenation, electrochemical, and carboxylation reactions. Reactions where CO_2 is used as an oxidant were also shown in Table 2.2. In Table 2.3, various catalytic reactions of CO_2 are listed that produce industrially important chemicals (Song, et al., 2002, Creutz and Fujita, 2000, Steinberg, et al., 1999, Inui, et al., 1998, Sullivan, 1993, and Inoue and Yamazaki, 1982).

Table 2.2 Chemical Synthesis from CO_2 from Various Sources (Xu, 2003)

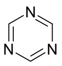
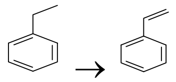
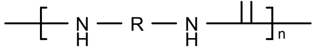
CO_2 hydrogenation
$CO_2 + H_2 \rightarrow CH_4$ $CO_2 + H_2 \rightarrow C_nH_{2n+2}$ or C_nH_{2n} $CO_2 + H_2 + NH_3 \rightarrow C_nH_{2n+1}NH_2$ or $HCONH_2$ or  $CO_2 + H_2 + HY \rightarrow HCOY + H_2O$ $CO_2 + H_2 \rightarrow C + H_2O$ $CO_2 + H_2 \rightarrow CH_3CH_2OH$
CO_2 used as oxidant (oxygen provider)
$CO_2 + C_3H_8 \rightarrow C_3H_6$ $CO_2 + CH_4 \rightarrow CO$ $CO_2 + 2NH_3 \rightarrow CO(NH_2)_2 + H_2O$ $CO_2 +$  $CO_2 + H_2N-R-NH_2 \rightarrow$  $-[NH-R-NH-C(=O)]_n-$

Table 2.2 (Continued).

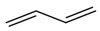
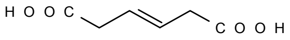
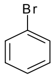
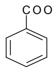
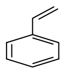
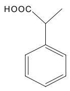
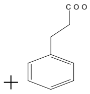
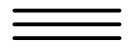
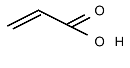
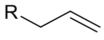
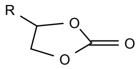
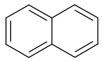
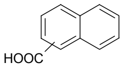
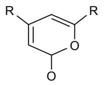
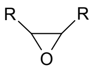
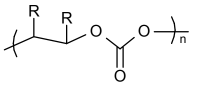
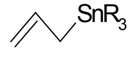
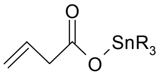
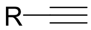
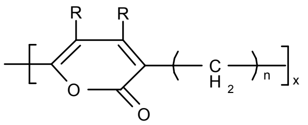
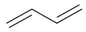
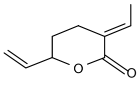
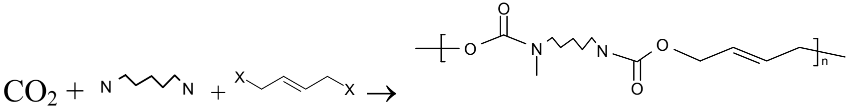
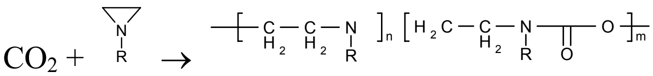
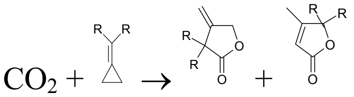
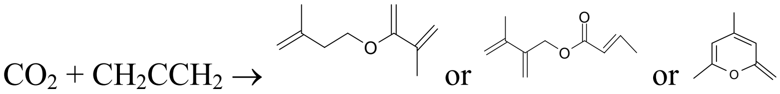
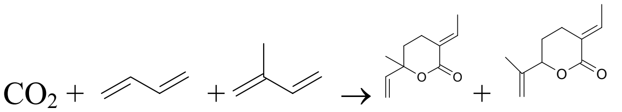
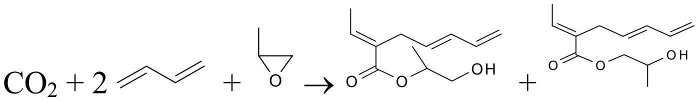
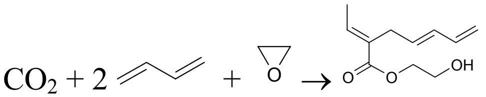
CO_2 electrochemical reaction
$CO_2 + 2e^- + 2H^+ \rightarrow HCOOH$
$CO_2 + 2e^- \rightarrow CO$
$CO_2 + 4e^- + 4H^+ \rightarrow CH_3OH$
$CO_2 + 4e^- + 4H^+ \rightarrow CH_4$
$CO_2 + 12e^- \rightarrow C_2H_4$
$CO_2 + 2e^- + 2H^+ +$  $\rightarrow$ 
$CO_2 + 2e^- + 2H^+ +$  $\rightarrow$ 
$CO_2 + 2e^- + 2H^+ +$  $\rightarrow$  + 
$CO_2 + 2e^- + 2H^+ +$  $\rightarrow$ 
CO_2 carboxylation (CO_2 insertion)
$CO_2 + ROH + R_2NH \rightarrow HCOOR + HCONR_2$
$CO_2 + C_2H_4 + H_2O \rightarrow CH_3CH(OH)COOH$
$CO_2 + C_6H_5ONa \rightarrow C_6H_5(COONa)OH$ $\xrightarrow{H^+} C_6H_5(COOH)OH$ $\xrightarrow{(CH_3CO)_2O} C_6H_5(COOCH_3)COOH$
$CO_2 +$  $+ O_2 \rightarrow$ 
$CO_2 +$  $\rightarrow$ 
$CO_2 +$ RC≡CR $\rightarrow$ 
$CO_2 + RNH_2 + R'X \rightarrow RNHCOOR'$
$CO_2 +$  $\rightarrow$ 
$CO_2 +$  $\rightarrow$ 
CO_2 carboxylation (CO_2 insertion) (Continued)
$CO_2 + CH_4 \rightarrow CH_3COOH$
$CO_2 + ROH \rightarrow ROCOOR$
$CO_2 + 2$ $\rightarrow$ 
$CO_2 +$  $\rightarrow$ 

Table 2.2 (Continued).



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

$CO_2 + C_2H_4 \rightarrow CH_3CH_2COOH + CH_3CH_2COOC_2H_5$





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

Hydrogenation reactions produce alcohols, hydrocarbon synthesis reactions produce paraffins and olefins, and amine synthesis reactions produce methyl and higher order amines. Hydrolysis reactions can produce alcohols and organic acids. Carbon dioxide serves as an oxygen source in the ethylbenzene to styrene reaction. It can be used in dehydrogenation and reforming reactions. A reaction for producing graphite from CO_2 by hydrogenation was also given in Table 2.3.

A detailed review of the literature for the reactions of carbon dioxide is described below for the reactions in Table 2.3. The operating conditions like temperature and pressure, catalyst used, reactant conversion, and the reaction products of these experimental studies are given. These experimental studies will be discussed in more detail in Chapter Three.

Table 2.3 Catalytic Reactions of Carbon Dioxide from Various Sources. (Hertwig, et al., 2002)

Hydrogenation:	
● $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$	Methanol
● $2CO_2 + 6H_2 \rightarrow C_2H_5OH + 3H_2O$	Ethanol
● $CO_2 + H_2 \rightarrow CH_3OCH_3$	Dimethyl Ether
Hydrocarbon Synthesis:	
● $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	Methane and higher HC
● $2CO_2 + 6H_2 \rightarrow C_2H_4 + 4H_2O$	Ethylene and higher olefins
Carboxylic Acid Synthesis:	
● $CO_2 + H_2 \rightarrow HCOOH$	Formic Acid
● $CO_2 + CH_4 \rightarrow CH_3COOH$	Acetic Acid
Graphite Synthesis:	
● $CO_2 + H_2 \rightarrow C + H_2O$	Graphite
● $CH_4 \rightarrow C + H_2$ $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	
Amine Synthesis:	
● $CO_2 + 3H_2 + NH_3 \rightarrow CH_3NH_2 + 2H_2O$	Methylamine and higher amines
Hydrolysis and Photocatalytic Reduction:	
● $CO_2 + 2H_2O \rightarrow CH_3OH + O_2$	Methanol
● $CO_2 + H_2O \rightarrow HCOOH + \frac{1}{2} O_2$	Formic Acid
● $CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$	Methane
Other Reactions:	
● $C_6H_5C_2H_5 + CO_2 \rightarrow C_6H_5C_2H_3 + CO + H_2O$	Styrene
● $CO_2 + C_3H_8 \rightarrow C_3H_6 + H_2 + CO$	Propylene
● $CO_2 + CH_4 \rightarrow 2CO + H_2$	Reforming

*** Methanol**

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta HE = -49.3 \text{ kJ/mol}, \Delta GE = +3.48 \text{ kJ/mol}$$

● Cu-Zn-Cr-Al mixed oxide catalyst (CuO: ZnO: Cr_2O_3: Al_2O_3 = 25: 41.5: 1.2: 32.3 wt%), space velocity of 4700 h^{-1}, 50 atm pressure, 523 K, 21.2% conversion to methanol, H_2/CO_2 = 75/25, 355 g/l.h Space-time yield of methanol. (Inui, 2002)

● Cu-Zn-Cr-Al mixed oxide catalyst (CuO: ZnO: Cr_2O_3: Al_2O_3 = 25: 41.5: 1.2: 32.3 wt%), space velocity of 4700 h^{-1}, 80 atm pressure, 523 K, 28.5% conversion to methanol, H_2/CO_2 = 75/25, 477 g/l.h Space-time yield of methanol. (Inui, 2002)

● Cu-Zn-Cr-Al mixed oxide catalyst (CuO: ZnO: Cr_2O_3: Al_2O_3: Ca_2O_3 = 38.1: 29.4: 1.6: 13.1: 17.8 wt%, Pd 1 wt%), space velocity of 18,800 h^{-1}, 80 atm pressure, 563K, 25.1% conversion to methanol, H_2: CO_2: CO = 75: 22: 3, 1,483 g/l.h space-time yield of methanol. (Inui, 2002)

● Four component composite catalyst (CuO: ZnO: Cr_2O_3: Al_2O_3: Ga_2O_3: Pd = 37.7: 29.1: 1.6: 13.0: 17.6: 1 wt%), space velocity of 18,000 h^{-1}, 543K, 22% methanol selectivity, 26.1% CO_2 conversion, 0.2% HC selectivity, 3.9% CO selectivity, reaction gas is 22% CO_2, 3% CO, 75% H_2. (Inui, 2002)

● Ni/Cu(100) catalyst, UHV/high pressure cell apparatus, 1.5 bar, 543 K, 30 mbar CO_2, 1370 mbar H_2 and 100 mbar CO feed gas composition, rate of formation of methanol in TOF is $60x10^{-6}(\text{Ni site})^{-1}(s)^{-1}$. (Nerlov, et al., 1999)

● Cu-Mn catalysts supported on $ZnrO_2$ and TiO_2, flow type fixed bed reactor, 250 ºC, 10 atm, feed gas $H_2/CO/CO_2/N_2$ = 60/30/5/5. (Omata, et al., 2002)

● Raney Cu-Zr catalyst, flow reactor, 523 K, 5 MPa, CO_2/H_2 = 1/3, SV = $18000h^{-1}$, 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, 250EC, 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)

● Multicomponent $Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3$ catalyst, production capacity 50 kg/day, tube reactor, 523K, 5 MPa, H_2/CO_2 = 3/1, 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)

● Fe 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 ºC, 5 MPa, 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 = $10000h^{-1}$. (Bonivardi, et al., 1998)

- 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, 270^0 C, 80 atm, SV = $18,800h^{-1}$, $CO_2/CO/H_2$ = 22/3/75, conversion to methanol = 22%. (Hara, et al., 1998)

- $Cu/ZnO/Al_2O_3$ catalyst, packed-bed reactor, $H_2/CO_2 = 3/1$, 20 bar, SV = 4500 h^{-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 = $5000h^{-1}$, recycle ratio = $4m^3N/m^3N$, CO_2 conversion = 95% for 3000 hours. (Hirano, et al., 1998)

*** Ethanol**

$$2CO_2 + 6H_2 \rightarrow C_2H_5OH + 3H_2O \qquad \Delta HE = -173.3 \text{ kJ/mol}, \Delta GE = -64.95 \text{ kJ/mol}$$

- Rh-Li/SiO_2 catalysts, ethanol selectivity of 15.5% and a CO_2 conversion of 7%, 5 MPa pressure and 513 K operating temperature, feed ration $H_2/CO_2 = 3$, flow-rate of 100 cm^3/min, reaction mechanism involves intermediate CO formation. (Kusama, et al., 1996)

- Rh-Li-Fe/SiO_2 catalyst, 69 atm pressure, 573 K temperature, 10.5% conversion of CO_2, 10.5% selectivity to ethanol. (Inui, 2002)

- Cu-Zn-Fe-K catalyst, 49 atm pressure, 513-533 K temperature range, 21.2% conversion of CO_2, 21.2% selectivity to ethanol. (Inui, 2002)

- Fe-Cu-Zn-Al-K catalyst, 20,000 h^{-1} space velocity, 80 atm pressure, 583 K, 28.5% conversion of CO_2, 28.5% selectivity to ethanol. (Inui, 2002)

- (Rh/MFI-silicate)-(Fe-Cu-Zn-Al-K) catalyst packed in series, 70,000 h^{-1} space velocity, 80 atm pressure, 623 K, 12.8% conversion of CO_2, 12.8% selectivity to ethanol. (Inui, 2002)

- (Fe-Cu-Al-K) (Cu-Zn-Al-K.Ga.Pd) catalysts physically mixed, 50,000 h^{-1} space velocity, 80 atm pressure, 603 K, 25.1% conversion of CO_2, 25.1% selectivity to ethanol. (Inui, 2002)

- [Rh_{10}Se]/TiO_2 catalyst, reaction carried in a closed circulation system (dead volume 210 cm^3), 523 K reaction temperature, 623 K evacuation temperature, 47kPa pressure, ethanol synthesis rate $1.9/10^{-3}molh^{-1}g_{cat}^{-1}$, by products (methane + CO) $0.4/10^{-3}molh^{-1}g_{cat}^{-1}$, 83% ethanol selectivity. (Izumi, et al., 1998)

● 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, $H_2/CO_2 = 3/1$, 1.8% CO, 10ml/min, main products are CH_4, CO, C_2H_5OH, 16% ethanol selectivity, 40% CH_4 selectivity, 38% CO selectivity. (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, 54.5% overall CO_2 conv, and about 5% CO_2 conversion to ethanol. (Yamamoto, et al., 1998)

● K/Cu-Zn-Fe-Cr oxides catalyst, conventional flow reactor, 300°C, 7.0MPa, 35% CO_2 conversion and 16% ethanol selectivity. (Higuchi, et al., 1998)

● K/Cu-Zn-Fe oxides catalyst, conventional flow reactor, 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)

*** Dimethyl Ether**

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

$$\text{Total: } CO_2 + 3H_2 + CH_3OH \rightarrow CH_3OCH_3 + 2H_2O \quad \Delta HE = -73.2 \text{ kJ/mol}$$

$$\Delta GE = -13.1 \text{ kJ/mol}$$

● γ-Al_2O_3 catalyst modified with 1 wt% silica for the second reaction and methanol synthesis catalyst for the first reaction, fixed bed reactor, 523 K, partial pressure of methanol = 101.2 torr, 70% methanol conversion. (Jun, et al., 2002)

● Cu-ZnO-Al_2O_3-Cr_2O_3 + H-ZSM-5 ($SiO_2/Al_2O_3 = 80$) stable hybrid catalyst, co-production of DME and methanol, high activity of catalyst, 523 K, 3.0 MPa, yield of DME and methanol higher than 26%, over 90% DME selectivity. (Tao, et al., 2001)

● 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)

*** Methane, Ethane, Ethylene, and Higher Olefins**

● Calcium based binary catalysts (CeO_2, Cr_2O_3 or MnO_2 with $Ca(NO_3)_2$), fixed bed reactor, ambient pressure, 800°C, 15% C_2H_6 yield, 25% C_2H_4 yield, $CO_2/CH_4 = 2$. (Wang and Ohtsuka, 2002)

$$2CH_4 + CO_2 \rightarrow C_2H_6 + CO + H_2O \quad \Delta HE = 106.4 \text{ kJ/mol}, \Delta GE = 97.6 \text{ kJ/mol}$$

$$2CH_4 + 2CO_2 \rightarrow C_2H_4 + 2CO + 2H_2O \quad \Delta HE = 284 \text{ kJ/mol}, \Delta GE = 226.6 \text{ kJ/mol}$$

- Amorphous Ni-Zr-rare earth element catalyst (Ni-30Zr-10Sm), fixed bed flow reactor, CO_2/H_2 = 1/4, F/W = 5,400 $ml \cdot g^{-1}h^{-1}$, 473K, CO_2 conversion = 98%. (Habazaki, et al., 1998)

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ $\Delta H^o = -165$ kJ/mol, $\Delta G^o = -113$ kJ/mol
$2CO_2 + 6H_2 \rightarrow C_2H_4 + 4H_2O$ $\Delta H^o = -128$ kJ/mol, $\Delta G^o = - 57$ kJ/mol
$2CO_2 + 7H_2 \rightarrow C_2H_6 + 4H_2O$ $\Delta H^o = -264$ kJ/mol, $\Delta G^o = -158$ kJ/mol
$3CO_2 + 9H_2 \rightarrow C_3H_6 + 6H_2O$ $\Delta H^o = -250$ kJ/mol, $\Delta G^o = -126$ kJ/mol
$3CO_2 + 10H_2 \rightarrow C_3H_8 + 6H_2O$ $\Delta H^o = -374$ kJ/mol, $\Delta G^o = -212$ kJ/mol

- Fe-Cu-Na with US-Y catalyst, 250°C, 20atm, SV = 3000 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)

- 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)

- Fe-Zn-Zr/HY catalyst, fixed-bed flow reactor, 360°C, 5MPa, SV = 3000 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)

- Fe-ZnO/HY catalyst, fixed bed flow reactor, 350°C, 50 atm, SV = 3,000ml/g-cat·h, H_2/CO_2 = 3, 6 hours, CO_2 conversion = 13.3%, C_{2+} yield = 4.5, ethylene selectivity = 90%. (Souma, et al., 1998)

- Fe-K/KY zeolite catalyst, fixed bed reactor, 573K, 10atm, H_2/CO_2 = 3/1, CO_2 conversion for total hydrocarbons = 21.28%, C_2H_4 distribution in total hydrocarbons = 9.12%, olefins selectivity = 82.38 C-mol%. (Kim, et al., 1998)

- Carbon supported Co catalysts, two-step reaction sequence, 350 - 450°C for 1st reaction, and 100°C for 2nd reaction, fixed bed reactor. (Zhang, et al., 2002)

$$2CH_4 \rightarrow CH_x + H_2$$
$$CH_x + H_2 \rightarrow C_2H_6 + C_2H_8$$

- 1st reactor – (37.7% Cu, 29.1% ZnO, 1.6% Cr_2O_3, 13% Al_2O_3, 17.6% Ga_2O_3, 1% Pd) catalyst, feed gas 22% CO_2, 3% CO, 75% H_2, 543 K, 7.8 MPa, 18,800 h^{-1} space velocity, 22% conversion to methanol, 1410 g/l.h space time yield, two-stage series reactors, 2nd reactor – H-Ga-Silicate catalyst, 1.5 MPa, 573 K, 100% methanol conversion, 53.6% gasoline selectivity. (Inui, 2002)

$CO_2 + CO + 5H_2 \rightarrow 2CH_3OH + H_2O$ $\Delta H^o = -139.8$ kJ/mol, $\Delta G^o = -21.7$ kJ/mol
$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$ $\Delta H^o = -23.9$ kJ/mol, $\Delta G^o= -16.6$ kJ/mol
$CH_3OCH_3 \rightarrow H_2C=CH_2 + H_2O$ $\Delta H^o = -5.2$ kJ/mol, $\Delta G^o= -47.6$ kJ/mol
$H_2C=CH_2 + CH_3OH \rightarrow CH_2=CH\text{-}CH_3 + H_2O \Delta H^o = -73.3$ kJ/mol, $\Delta G^o= -71.9$ kJ/mol

● a($Zn_aCr_bCu_cK_d$-O_x)/b[Fe_3+/ZSM-11] catalyst, CO_2 hydrogenation, flow-type reactor, 653 K, 3.0 MPa, 1500 h^{-1} volumetric rate of gaseous mixture, 64.2% hydrocarbon conversion, 57.3% selectivity for hydrocarbons of the petrol fraction. (Lunev, et al., 1999)

$$CO_2 + H_2 \rightarrow \text{liquid hydrocarbons}$$

● Mn/g-Al_2O_3 catalyst, reaction of isobutane and CO_2, 735 - 840°C reaction temperature, $C_2 – C_4$ alkene yield of 36 – 58%. (Macho, et al., 1997)

$$C_4H_{10} + CO_2 \rightarrow CO + H_2, CO, C_2H_4, C_3H_6, C_4H_8$$

*** Formic Acid**

$$CO_2\ (g) + H_2\ (g) \rightarrow HCOOH\ (l) \qquad \Delta HE = -31\ kJ/mol, \Delta GE = 33\ kJ/mol$$

● RuCl(O_2CMe)(Pme_3)$_4$ catalyst, CO_2 hydrogenation, 40 bar H_2, 60 bar CO_2, 2.5 mmol methanol, 3.6 mmol NEt_3 and 3.0 m mol catalyst (reaction components), 50°C, 3500 h^{-1} rate. (Thomas, et al., 2001)

● Rhodium catalyst, autoclave, 25°C, 40 bar, H_2/CO_2 = 1/1, 12 hours, 3440 mol formic acid per mol Ru. (Dinjus, 1998)

*** Acetic Acid**

$$CH_4 + CO_2 \quad \rightarrow CH_3COOH \quad \Delta HE = 35.9\ kJ/mol, \Delta GE = 70.7\ kJ/mol$$

● VO(acac)$_2$ catalyst, autoclave, $K_2S_2O_8$ 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)

● 5% Pd/C catalyst, RGIBBS reactor in AspenPlus, 100 - 500EC, 10 - 150 atm, inlet concentration CH_4/CO_2 = 95/5. (Spivey, et al., 1999)

● $K_2S_2O_8$, VO(acac)$_2$ catalyst, glass-lined autoclave, 80°C, 80 psig CH_4, 120 psig CO_2, 40% yield of acetic acid based on methane conversion. (Zerella, et al., 2003)

*** Styrene**

$$C_6H_5C_2H_5 + CO_2 \rightarrow C_6H_5C_2H_3 + CO + H_2O\ \Delta HE= 159.2\ kJ/mol, \Delta GE= 111.8\ kJ/mol$$

● Vanadium oxide –loaded MgO (V/MgO-100A) catalyst, fixed bed flow type quartz reactor, 1 atm pressure, 550°C, 59.1% ethylbenzene conversion, 53.8% styrene yield, 91.1% styrene selectivity. (Sakurai, et al., 2000)

- 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 = 100%, yield of styrene = 70%, energy requirement = 6.3×10^8 cal/t-styrene (1.5×10^9 cal/t-styrene for commercial process using steam). (Mimura, et al., 1998)

* 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 = 23%, and C_3H_8 conversion = 45%. (Takahara, et al., 1998)

$$C_3H_8 + CO_2 \rightarrow C_3H_6 + CO + H_2O \quad \Delta HE = 165 \text{ kJ/mol}, \Delta GE = 114.8 \text{ kJ/mol}$$

- proprietary platinum catalyst (DeH-14), 98 wt% propane, 600°C and 1 atm, propylene main product, hydrogen by-product, selectivity to propylene 85%, 40% propane conversion per pass. (C & EN, June 2003, p.15)

$$C_3H_8 \rightarrow C_3H_6 + H_2 \quad \Delta H^o = 124 \text{ kJ/mol}, \Delta G^o = 86 \text{ kJ/mol}$$

* Graphite

- WO_3 or Y_2O_3 catalyst, direct hydrogenation process, 0.1 MPa, 700EC, W/F = 10g-cat.h/mol, 40% graphitic carbon selectivity, 60% CO2 conversion, feed ratio $H_2/CO_2/N_2$ = 2/1/5. (Arakawa, 1998)

- 1000°C, 10 kbar, CO_2 in supercritical state, raw materials are 2.6g dry ice, 0.3g Mg, 1.217g solid product after reaction, 110 mg final product after purification, 15 wt% yield of NT. (Motiei, et al., 2001)

$$Mg_{(g)} + CO_{2(g)} \rightarrow MgO_{(g)} + CO_{(gas)}$$
$$Mg_{(l)} + CO_{(g)} \rightarrow MgO_{(g)} + C_{(graphite)}$$
$$\text{Global Reaction: } Mg_{(g)} + Mg_{(l)} + CO_{2(g)} \rightarrow 2\,MgO_{(g)} + C_{(graphite)}$$

- Nickel supported on SiO_2 catalyst, membrane reactor, 1 atm, 500°C, feed ratio $H_2/CO_2/N_2$ = 4/1/3, 70% CO_2 reduced to graphite carbon. (Nishiguchi, et al., 1998)

$$2CH_4 \rightarrow 2C + 4H_2$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$
$$\text{Total: } CH_4 + CO_2 \rightarrow 2C + 2H_2O \quad \Delta HE = -15.5 \text{ kJ/mol}, \Delta GE = -12.33 \text{ kJ/mol}$$

* Methylamines and Higher Amines

$$CO_2 + H_2 \rightarrow CO + H_2O \quad \Delta HE = 41 \text{ kJ/mol}, \Delta GE = 29 \text{ kJ/mol}$$
$$CO + 2H_2 \rightarrow CH_3OH \quad \Delta HE = -90 \text{ kJ/mol}, \Delta GE = -25 \text{ kJ/mol}$$
$$CH_3OH + NH_3 \rightarrow CH_3NH_2 + H_2O \quad \Delta HE = -17 \text{ kJ/mol}, \Delta GE = -17 \text{ kJ/mol}$$

$$CH_3OH + CH_3NH_2 \rightarrow (CH_3)_2NH + H_2O \qquad \Delta HE = -37 \text{ kJ/mol}, \Delta GE = -30 \text{ kJ/mol}$$

● Cu/Al_2O_3 catalysts, 51 wt% Cu/Al_2O_3, 0.6 MPa, 277EC, GHSV = 3000/h, CO by-product, feed ratio $H_2/CO_2/NH_3 = 3/1/1$. (Arakawa, 1998)

*** Hydrolysis and Photocatalytic reduction**

$$2CO_2 + 4H_2O \rightarrow 2CH_3OH + 3O_2 \qquad \Delta HE = 1352.3 \text{ kJ/mol}, \Delta GE = 1378.6 \text{ kJ/mol}$$
$$CO_2 + 2H_2O \rightarrow CH_4 + 2O_2 \qquad \Delta HE = 802.6 \text{ kJ/mol}, \Delta GE = 801.1 \text{ kJ/mol}$$

● TiO_2 catalysts, UV- irradiation of active TiO_2 catalysts, 275 K, CH_4 and CH_3OH major products, feed gases 0.12mmol CO_2 and 0.37 mmol H_2O, irradiation time 6h, 3.50 ev band gap, 0.17 mmol h^{-1} g^{-1} CH_4 yield. (Yamashita, et al., 2002)

*** Polymerization Reactions**

Polyethercarbonate:

$$C_3H_6O + C_6H_{10}O + CO_2 \rightarrow - [CO_2 - C_3H_6O]_n - [CO_2 - C_6H_{10}O]_m -$$

● Yttrium – metal coordination catalyst, copolymerization of CO_2, propylene oxide and cyclohexene oxide, 353 K and 27.2 atm, autoclave equipped with a magnetic stirrer, 1000 rpm spinning speed. (Tan, et al., 2002)

*** Photoelectric and Electrochemical Reactions**

● 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)

$$CO_2 + H_2 \rightarrow CH_4, C_2H_4, C_2H_5OH$$

● 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)

$$CO_2 + H_2 + H_2O \rightarrow HCOOH, CH_3OH, CH_3\text{-}CHOH\text{-}COOH \text{ (lactic acid)}$$

● 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)

$$CO_2 + H_2 \rightarrow C_2H_5OH, CO, HCOO^-$$

● 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)

$$CO_2 + H_2 \rightarrow HCOOH, CO$$

● 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)

$$CO_2 + H_2O \rightarrow CH_4, CH_3OH$$

● 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)

$$CO_2 + H_2 + H_2O \rightarrow HCOOH, CH_4, C_2H_4$$

● 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% respectively. (Shiratsuchi, et al., 1998)

$$CO_2 + H_2 + H_2O \rightarrow CH_4, C_2H_4, C_2H_5OH, CH_3CHO, HCOOH$$

● 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., 1998)

$$CO_2 + H_2 \rightarrow CH_4 , CO$$

*** CO_2 Reforming of Methane**

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \quad \Delta HE = 247 \text{ kJ/mol}, \Delta GE = 170.6 \text{ kJ/mol}$$

● Rh – modified Ni – Ce_2O_3 –Pt catalyst (10 wt% Ni – 6 wt% Ce_2O_3), feed gas 10 mol% CH_4, 10 mol% CO_2 and 80 mol% N_2, 73,000 h^{-1} space velocity, 873 K, 65% CH_4 conversion. (Inui, 2002)

● Rh – modified four –component catalyst, propane addition in CO_2 reforming of methane, 73,000 h^{-1} space velocity, 35% CH_4 – 10% CO_2 – 3.3% C_3H_8 – 16.5% 0_2 – 35.2% N_2 feed gas composition, 700°C catalyst-bed temperature, 500°C furnace temperature, 1 atm pressure, 80.8% CH_4 conversion. (Inui, 2002)

● Rh – modified four –component catalyst, ethane addition in CO_2 reforming of methane, 73,000 h^{-1} space velocity, 35% CH_4 – 10% CO_2 – 5% C_2H_6 – 17.5% 0_2 – 32.5% N_2 feed gas composition, 700°C catalyst-bed temperature, 500°C furnace temperature, 1 atm pressure, 82.2% CH_4 conversion. (Inui, 2002)

● Tungsten Carbide catalyst, fixed bed reactor, 850°C, 1 atm pressure, 90.7% methane conversion, 99.7% carbon dioxide conversion, 86.6% yield of carbon monoxide, H_2/CO

products ratio of 1.1, CO_2/CH_4 =1.15 feed gas ratio, space velocity of 5040 $cm^3.g^{-1}.h^{-1}$. (Shamsi, 2002)

● Ni based catalysts (R-67), fixed bed reactor, 750°C, 1 atm pressure, 94.2% CH_4 conversion, 91.1% CO_2 conversion, 95.3% CO yield, H_2/CO products ratio of 1.0, CO_2/CH_4 = 1.1 feed gas ratio, space velocity of 5040 $cm^3.g^{-1}.h^{-1}$. (Shamsi, 2002)

● 1% Rh/alumina catalyst, fixed bed reactor, 850°C, 1 atm pressure, space velocity of 5040 $cm^3.g^{-1}.h^{-1}$, H_2/CO products ratio of 1.0, 95.7% CO yield, 97.2% CH_4 conversion, 97.4% CO_2 conversion. (Shamsi, 2002)

● Ni supported ultra fine ZrO_2 catalyst, fixed bed quartz tubular reactor, 1030 K, 1 atm pressure, CH_4/CO_2 =1.0 feed ratio, space velocity of 24,000 ml/h.g-cat, 86.2% CH_4 conversion, 88.3% CO_2 conversion, CO/H_2 = 1.2 product ratio, 95.4% CO selectivity, 79.5% H_2 selectivity. (Wei, et al., 2002)

● Ru loaded La_2O_3 catalysts, fixed bed flow type quartz reactor, 600°C, 1 atm pressure, CH_4/CO_2 = 1.0, space velocity of $36{,}000h^{-1}mLg\text{-}cat^{-1}$, 28% CH_4 conversion, 33% CO_2 conversion, 25.4% H_2 yield, 30.5% CO yield, H_2/CO = 0.83 product ratio. (Nakagawa, et al., 2002)

● Ru loaded Y_2O_3 catalysts, fixed bed flow type quartz reactor, 600°C, 1 atm pressure, CH_4/CO_2 = 1.0, space velocity of $36{,}000h^{-1}mLg\text{-}cat^{-1}$, 29.9% CH_4 conversion, 35.5% CO_2 conversion, 27.1% H_2 yield, 32.7% CO yield, H_2/CO = 0.83 product ratio. (Nakagawa, et al., 2002)

● 8 wt% Ni/Na-Y catalyst, 750°C, 1 atm pressure, CH_4/CO_2 =1.0 feed molar ratio, space velocity of 30,000 $cm^3.g^{-1}.h^{-1}$, 91.1% CO_2 conversion, 89.1% CH_4 conversion, 85.6% CO yield, 68.9% H_2 yield, H_2/CO = 0.80 product ratio. (Song, et al., 2002)

● 6.6 wt% Ni/Al_2O_3 catalyst, 750°C, 1 atm pressure, CH_4/CO_2 =1.0 feed molar ratio, space velocity of 30,000 $cm^3.g^{-1}.h^{-1}$, 91.8% CO_2 conversion, 95.3% CH_4 conversion, 81.9% CO yield, 66.3% H_2 yield, H_2/CO = 0.81 product ratio. (Song, et al., 2002)

● $Ni/SiO_2 - MgO$ catalyst, 700°C, 1atm pressure, CO_2/CH_4 = 0.84 feed ratio, fluidized bed reactor, H_2/CO = 0.69 product ratio, 37.7% CH_4 conversion, 52.7% CO_2 conversion. (Effendi, et al., 2002)

● Nickel-magnesia solid solution catalyst ($Ni_{0.03}Mg_{0.97}O$), fixed bed flow reaction system, CH_4/CO_2 = 1/1, 1123K, 0.1MPa, W/F = 1.2 gh/mol, methane conversion = 80%. (Tomishige, et al., 1998)

*** Dimethyl Carbonate**

$$2CH_3OH + CO_2 \rightarrow (CH_3O)_2CO + H_2O \qquad \Delta HE = -24 \text{ kJ/mol}, \Delta GE = -17 \text{ kJ/mol}$$

- Phosphoric acid-modified Zirconia catalysts (H_3PO_4/ZrO_2), stainless steel autoclave reactor, 192 mmol CH_3OH, 200 mmol CO_2, 0.5 g catalyst used, 4 Mpa pressure, 383-443 K temperature, DMC selectivity > 99%. (Ikeda, et al., 2002)

*** Formaldehyde**

$$CO_2 + H_2 \rightarrow HCHO \qquad \Delta HE = 284.9 \text{ kJ/mol}, \Delta GE = 292 \text{ kJ/mol}$$

- PtCu/SiO_2 catalyst, CO_2 hydrogenation, 423 K, 600 kPa, formaldehyde main product, Pt/Cu = 0.03. (Lee, et al., 2001)

*** CO_2 as a Solvent**

Cycloalkanes:

$$C_6H_{10}(l) + H_2 \xrightarrow[\text{(supercritical } CO_2)]{Pd/C} C_6H_{12}(l) \qquad \Delta HE = -117.9 \text{ kJ/mol}, \Delta GE = -74.9 \text{ kJ/mol}$$

- Pd/C catalyst, continuous fixed-bed reactor, 343 K and 13.6 Mpa, equimolar feed of reactants (cyclohexene and hydrogen) in 90% CO_2, olefin space velocity 20 h^{-1}, cyclohexane productivity 16 Kg/Kg cat/h, 2% loss in conversion per hour. (Arunajatesan, et al., 2001)

- Cyclohexene hydrogenation in supercritical CO_2, 70°C, 136 bar pressure, space velocity of 20 h^{-1}, 80% conversion to cyclohexane, 100% selectivity. (Bala Subramaniam, et al., 2002)

*** Supercritical CO_2 reactions**

- Dispersion polymerization of styrene in supercritical CO_2 to produce polystyrene (2.9 – 9.6mm) 370 bar, 65°C, polystyrene yield 85%, molecular wt. of the polymer 29.1 kg/mol, poly(1,1-dihydroperfluorooctyl acrylate) as a polymeric stabilizer, 20 w/v % styrene used, 85% styrene conversion. (Shiho *et. al.*, 2001)

- Reduction of fullerene particle size from 40 mm to 29 nm, raw materials CO_2 and N_2, buckminsters-fullerene (C_{60}), toulene and sodium dedecylbenzene sulfonate, C_{60} (40 mm) dissolved in toulene injected into supercritical CO_2, precipitation of C_{60} (29 nm) as fine particles, 50°C. (Chattopadhyay *et. al.*, 2000)

F) Chemical Complex and Cogeneration Analysis System

The objective of this Chemical Complex and Cogeneration Analysis System is to have a methodology to integrate new energy-efficient plants into the existing infrastructure of plants in a chemical production complex. The system gives corporate engineering groups new capability to design energy efficient and environmentally acceptable plants and have new products from greenhouse gases. This research will demonstrate this capability.

The system combines the Chemical Complex Analysis System, and the Cogeneration Analysis System. The Chemical Complex Analysis System determines the best configuration of plants in a chemical complex based on the AIChE Total Cost Assessment (TCA) for economic, energy, environmental and sustainable costs. It also incorporates EPA Pollution Index Methodology (WAR) algorithm. The Cogeneration Analysis System determines the best energy use based on economics, energy efficiency, regulatory emissions and environmental impacts from greenhouse gas emissions. The AIChE Total Cost Assessment (TCA) was described earlier in Chapter One.

The structure of the system is shown in Figure 2.1. The complex flowsheet is drawn, and material and energy balances, rate equations and equilibrium relations for the plants are entered through windows as equality constraints. These constraints are entered using the format of GAMS programming language that is similar to Excel and stored in an Access database. The production capacities, availability of raw materials, and demand of products are entered as inequality constraints, and are stored in the database.

The system takes the input equations in the database, and writes and runs a GAMS program to solve the mixed integer non-linear programming problem for the optimum configuration of the chemical complex. The information in the GAMS solution is presented to the user on the process flow diagram, on the cogeneration diagram, and in summary tables. These results can be exported to Excel, if desired.

The output of the system includes evaluating the optimum configuration of plants in a chemical production complex based on the AIChE Total Cost Assessment (TCA) for economic, energy, environmental and sustainable costs, and an integrated cogeneration sequential layer analysis. The integrated cogeneration sequential layer analysis determines cost effective improvements for individual plants using heat exchanger network analysis and cogeneration opportunities. These results are used to determine the optimum complex configuration and utilities integrated with the plants.

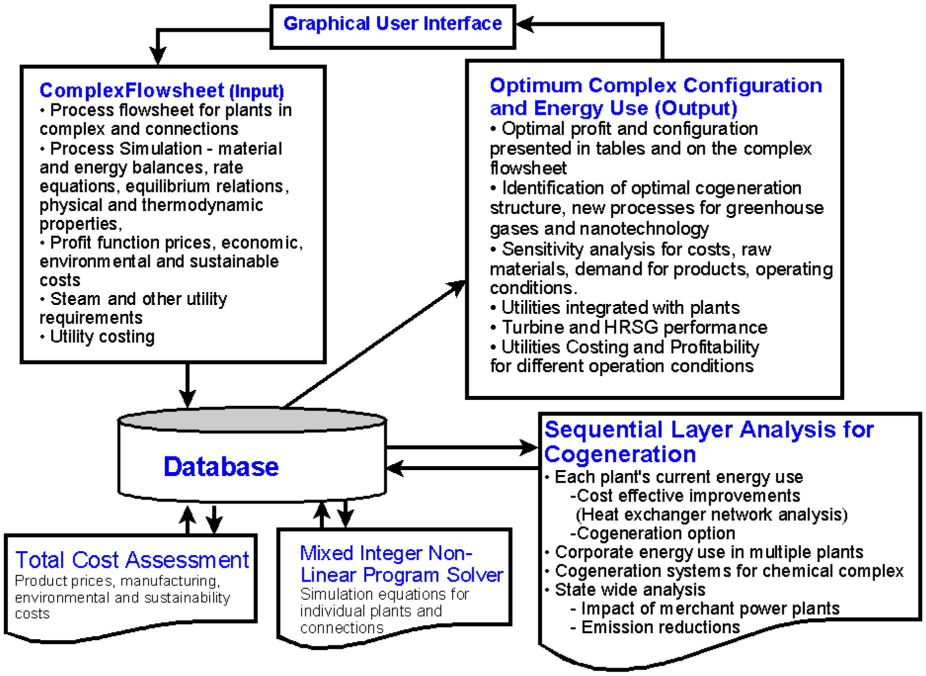


Figure 2.1. Structure of Chemical Complex and Cogeneration Analysis System (Hertwig, et al., 2000)

This technology is being used in the research to incorporate new plants that use greenhouse gases as raw materials in the existing chemical production complex in the Lower Mississippi River Corridor. The agricultural chemical complex in the Lower Mississippi River Corridor serves as a base case used with the system. A detailed description of the Chemical Complex and Cogeneration Analysis System is given by Xu, 2003. Also, the system with users manual and tutorial is available from the Minerals Processing Research Institute’s website, www.mpri.lsu.edu.

G) Summary

There have been five international conferences and numerous articles in the past twenty years on carbon dioxide reactions that consider using it as a raw material. The reactivity of carbon dioxide is due to the presence of π-electron density of the double bonds and the lone pairs of electrons on the oxygen atoms, or the electrophilic carbon atom (Keene, 1993). Reactions with carbon dioxide become thermodynamically more feasible if it is used as a co-reactant with other reactant that has higher (less negative) Gibbs free energy (Song, 2002). The physical and chemical properties of CO_2 were shown in Table 2.1.

The current largest use of carbon dioxide is the synthesis of urea. CO_2 can be used in hydrogenation reactions to produce alcohols, and in hydrocarbon synthesis reactions to produce paraffins and olefins. In Table 2.2, various reactions where CO_2 is used in the organic chemical synthesis are listed. The various catalytic reactions of CO_2 were listed in Table 2.3. Several new experimental studies involving the catalytic reactions were published in the recent decade. These experimental studies were briefly described earlier.

The Chemical Complex and Cogeneration Analysis System determines the best configuration of plants in a chemical production complex based on AIChE Total Cost Assessment (TCA) for economic, energy, environmental and sustainable costs. It also incorporates EPA Pollution Index Methodology (WAR) algorithm.

The material balances, rate equations and equilibrium relations are entered as equality constraints, and the production capacity, raw material availability, and product demand are entered as inequality constraints. The system takes the input equations in the database, and writes and runs a GAMS program to solve the mixed integer non-linear programming problem for the optimum configuration of the chemical complex. The output of the system includes evaluating the optimum configuration of plants in a chemical production complex based on the AIChE Total Cost Assessment (TCA) for economic, energy, environmental and sustainable costs, and an integrated cogeneration sequential layer analysis. This technology is being used in the research to incorporate new plants that use greenhouse gases as raw materials in the chemical production complex present in the Lower Mississippi River Corridor.

The experimental studies listed in this chapter will be discussed in more detail in Chapter Three. These experimental studies will be compared to the existing commercial processes. A methodology for the selection of new processes to be integrated in the chemical complex will be discussed in Chapter Three.

CHAPTER THREE: SELECTION OF NEW PROCESSES

The various reactions where carbon dioxide can be utilized as a raw material for the production of industrially important products were described in Chapter Two. For these reactions, there are nearly 100 published articles of laboratory experiments describing new methods and catalysts to produce these commercially important products (Hertwig, et al., 2003). The objective of this research is to identify and develop new energy efficient and environmentally acceptable processes that use carbon dioxide. The excess high purity carbon dioxide available from the chemical complex in the lower Mississippi River Corridor can be used as a raw material in these new processes.

The chemical production complex in the lower Mississippi River Corridor will be used to demonstrate the integration of these new plants into an existing infrastructure. Thus, potentially new processes are to be selected for being incorporated into the existing chemical production complex. The selected processes are simulated as industrial scale processes to estimate the energy requirements. The simulations of these processes are done using HYSYS. After the integration of these new processes, the Chemical Complex and Cogeneration Analysis System will be used to evaluate the energy and greenhouse gas reductions.

A methodology for selecting the new energy efficient processes was developed. New processes will be compared to the existing commercial processes. The criteria for selecting a new process include process-operating conditions such as pressure and temperature, and performance of the catalyst. Reactant conversion, product selectivity, cost of raw materials and products, and the thermodynamic feasibility of the reactions occurring in the process are also considered for selecting a new process for HYSYS simulation. If a new process demonstrates advantages over existing commercial process based on the above criteria, then that process is selected for HYSYS simulation. The criteria for selection of new processes will be explained further below.

The process conditions such as the operating temperature and operating pressure are the most important criteria for selecting a new process. A process operating at a lesser temperature and pressure than the conventional process will have the potential to reduce both operating costs and energy requirements.

The performance of catalyst includes its activity, time of deactivation, method of regeneration, and cost and availability of the catalyst. The reactant conversion and the selectivity to products are also functions of catalyst performance. If the catalyst used in the new process demonstrates a better performance than the commercial catalyst, then the new process will have the potential to operate at reduced energy requirements.

Pacific Northwest National Laboratory (PNNL) estimated potential energy savings for 26 commercial chemicals through improved catalysts (Pellegrino, 2000). The list of these commercial chemicals with estimated energy savings are shown in Table 3.1.

The next criterion that will be used for selection of new processes is the thermodynamic feasibility of reactions occurring in the processes. This will be based on the heat of reaction (ΔH^o), and the standard Gibbs free energies (ΔG^o) of the reactions. Negative values of ΔH^o indicate that a reaction is exothermic, i.e., heat is released; and positive values indicate that a reaction is endothermic, i.e., heat is absorbed. A process operating with an endothermic reaction requires energy be supplied for the reaction, there is a corresponding energy cost. On the other hand, if the process operates with an exothermic reaction, then energy is released, which can be removed and used effectively else where. Such a process will have the potential to reduce the total energy costs in a chemical complex.

Table 3.1. Potential Energy Savings through Improved Catalysts (Pellegrino, 2000)

Chemical	**Rank**	**Total Energy Savings (trillion BTUs)**	**Chemical**	**Rank**	**Total Energy Savings (trillion BTUs)**
Ammonia	1	294	Ethylene Dichloride	14	11
Propylene	2	98	Acetone	15	8
p-Xylene	3	94	Terephthalic Acid	16	8
Butadiene	4	81	Formaldehyde	17	6
Vinyl Chloride	5	44	Ethylbenzene	18	4
Methanol	6	37	Cumene	19	3
Ethylene Oxide	7	29	Acetic Acid	20	2
Acrylonitrile	8	24	Nitric Acid	21	1
Adipic Acid	9	20	MTBE	22	1
Styrene	10	20	Caprolactam	23	1
Vinyl Acetate	11	16	Ethylene Glycol	24	1
Propylene Oxide	12	16	Sulfuric Acid	25	1
Phenol	13	12	Isobutylene	26	0.3

According to Dodge, 1944, reactions are said to be less feasible as ΔG^o increases in a positive direction, but there is no definite value that can be chosen as clearly indicating that a reaction is not feasible from the standpoint of industrial operations. For example, the methanol synthesis reaction is + 11,000 cal/g-mole at 600K, and this reaction is certainly feasible. Dodge, 1944 provides the following guidelines for the purpose of ascertaining quickly and only approximately if any given reaction is promising at a given temperature.

If ΔG^o of a reaction is less than 0, then the reaction is said to be promising. If it is positive and is less than 10,000 cal/g-mole (42 kJ/g-mole), then the reaction is doubtful promise but warrants further study. If ΔG^o is further positive than 10,000 cal/g-mole, then the reaction is unfavorable and would be feasible only under unusual circumstances

(Dodge, 1994). The above guidelines are used in estimating the thermodynamic feasibility of a reaction while selecting the new processes.

There are certain ways to increase the conversion for reactions having positive ΔG^o. One standard procedure is to remove the products in an intermediate step. For example, this procedure is used in the double absorption contact process for sulfuric acid where sulfur trioxide is removed after the gas passes through two packed bed reactors before entering the last two reactors.

The next criterion will be used for selection of new processes is the cost of raw materials and products. For example, in certain CO_2 hydrogenation reactions, the conversion can be increased if H_2/CO_2 ratio is high (3-4). This implies that such a process requires more hydrogen, and hydrogen is an expensive raw material. Thus, such processes require more investment for raw materials.

On the other hand, if hydrogen is formed as a by-product in a new process, such a process could be incorporated into the chemical complex as it provides a source for expensive hydrogen. For example, a new process for propylene manufacture from propane produces hydrogen as a by-product. This potentially new process will be described later, and it provides a source for extra hydrogen that could be used in other processes.

Several new processes that use carbon dioxide for the production of industrially important products will be described. These new processes will be compared to the corresponding existing conventional processes. Processes that have advantages over the conventional process based on the selection criteria discussed above will be selected for HYSYS simulation.

A) Propylene

As mentioned earlier, Pacific Northwest National Laboratory (PNNL) estimated potential energy savings for 26 commercial chemicals through improved catalysts. Propylene is on this list with a potential energy savings of 98 trillion BTUs per year (Pellegrino, 2000). Propylene is produced commercially by using steam cracking of hydrocarbons. Two new processes are compared to the conventional process for propylene production, one from carbon dioxide and one from propane.

The conventional process for the manufacture of propylene is the steam cracking of hydrocarbons. It is obtained as a co-product with ethylene. Propane, naphtha, or gas oil is used as a feedstock (Speight, 2002). The flow diagram representing this process is shown in Figure 3.1. Typical capacities range from 30,000 to 1400,000 tonnes per year (Wells, 1999). The overall chemical reaction involved in the process using propane as feedstock is given below.

$$2C_3H_8 \rightarrow C_3H_6 + C_2H_4 + CH_4 + H_2 \quad \Delta H^o = 205.5 \text{ kJ/mol}, \Delta G^o = 127.5 \text{ kJ/mol}.$$

The above reaction is endothermic and requires substantial heat input. The hydrocarbon stream is heated with high-pressure steam before entering a tubular reactor. Heat recovered from the exit gases of tubular reactor is used to generate the required high-pressure steam. The reaction takes place at a temperature of 1023 – 1143K and at a pressure of 31 – 37 atm (Wells, 1999). The yield of propylene ranges from 14 – 18 percent and the ethylene ranges from 42 – 45 percent (Wells, 1999).

The mixture containing hydrogen and methane are separated in the demethanizer, and ethylene is recovered in a deethanizer tower by fractionation. Effluent from the base of deethanizer, which is a mixture of propane, propylene, propadiene (C=C=C) and propyne (C-C≡C) with traces of C_2 and C_4 hydrocarbons, passes to the depropanizer (Wells, 1999).

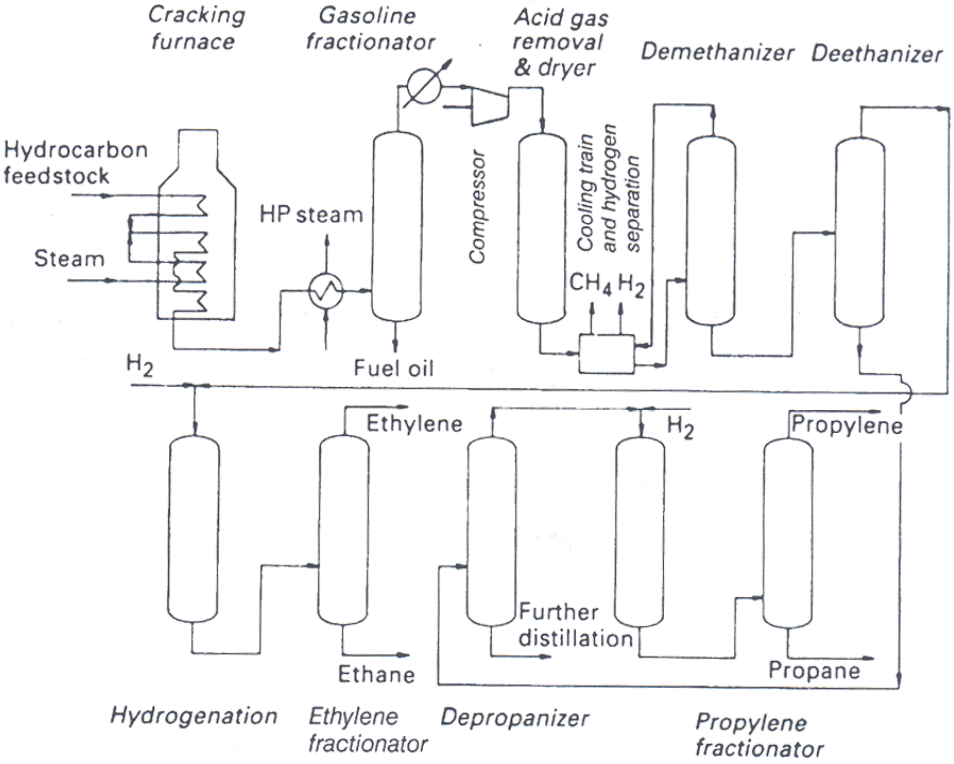


Figure 3.1. Propylene Production from Steam Cracking of Hydrocarbons, from Wells, 1999.

Hydrogen is added to convert propadiene (C=C=C) and propyne (C-C≡C) to propylene. The reaction is carried out in gas phase using a palladium catalyst at a temperature of 323 – 393K and at a pressure of 18 bar. Propylene is separated from propane in a single or double-column process using a reflux ratio between 0.90 – 0.97 (Wells, 1999).

Two new processes for propylene will be described. These processes will be compared to the conventional processes. The potential processes having advantages over the conventional processes will be selected for HYSYS simulation.

Takahara, et al., 1998, described results of an experimental study for the production of propylene by dehydrogenation of propane using carbon dioxide. The reaction was carried over Cr_2O_3/SiO_2 catalyst. The reaction involved in the process is given below.

$2C_3H_8 + CO_2 \rightarrow 2C_3H_6 + CO + H_2O + H_2$ $\Delta H^o = 289$ kJ/mol, $\Delta G^o = 201$ kJ/mol.

The above reaction is also endothermic and requires heat input. The reaction was carried out at a temperature of 823K and at a pressure of 1 atm. The yield and conversion to propylene observed were 10 percent and 45 percent respectively (Takahara, et al., 1998). The major by-products were CO and hydrogen. Presence of carbon dioxide enhanced the yield of propylene and suppresses catalyst deactivation (Takahara, et al., 1998).

A comparison of the conventional process and results of the experimental study led to the following observations. Both the processes are endothermic and energy needs to be supplied. However, the energy required for conventional process may be slightly less based on the standard heat of reaction. The conventional process operates at 1023 – 1143K and at 31-37 atm whereas the new process operates at 823K and 1 atm. Thus, this process is advantageous from the point-of-view of operating temperature and pressure. The yield of propylene in both the processes are comparable to each other.

Presence of carbon dioxide suppresses catalyst deactivation in the new process, and it uses carbon dioxide as a raw material that is obtained as excess in other processes. A separate reactor is required to convert propadiene to propylene, and addition of hydrogen. The cost of hydrogen is high, and also the production of by-product hydrogen is more in the new process.

The equipment required for the conventional process included cracking furnace, gasoline fractionator, compressor, demethanizer, deethanizer, ethylene fractionator, depropanizer and a propylene fractionator. The equipment for the new process requires three reactors and two distillation columns. In conclusion based on this comparison, this potentially new process is selected for HYSYS simulation.

The other potentially new process for propylene production will be described. Propylene can be produced from propane, but there are no plants in the lower Mississippi River Corridor that use this process. A new propylene plant built and operated by BASF Sonatrac PropanChem S.A. has started its trial operations at Tarragona, Spain (C & EN, June 2003, p.15). The $262 million plant has a production capacity of 350,000 metric tons per year of propylene, and is the first plant in Europe to use UOP LLC's C_3 Oleflex technology. This plant produces only propylene, and no by-product ethylene is produced. As only propylene is needed at the Tarragona site, it is more economical to use the propane dehydrogenation process than the conventional process (C & EN, June 2003, p.15). The use of steam cracking (conventional process) to produce the same amount of propylene costs three to four times as much as Oleflex (C & EN, June 2003, p.15). At a propane price of $180 per metric ton, the cost of production is $265 per metric ton of polymer-grade propylene. Propylene is produced in this process according to the following reaction.

$$C_3H_8 \rightarrow C_3H_6 + H_2 \qquad \Delta H^o = 124 \text{ kJ/mol}, \Delta G^o = 86 \text{ kJ/mol}.$$

The propane feedstock containing 98 wt% propane is heated in excess of 600°C and fed to the reactors, which operate slightly above atmospheric pressure. The dehydrogenation reaction is carried over a proprietary platinum catalyst from UOP, called

DeH-14. The selectivity to propylene is above 85% and propane conversion per pass is about 40% (C & EN, June 2003, p.15).

During product recovery, the reactor effluent is cooled, compressed and dried. Hydrogen is recovered at 90-93 mol% purity. Separator liquid is sent to a selective hydrogenation unit where a small quantity of hydrogen reacts with diolefins and acetylenes over a Pd catalyst. The reactor effluent goes to a deethanizer and propane-propylene splitter to produce a chemical or polymer-grade propylene (C & EN, June 2003, p.15). Unconverted propane, which is in excess of 60% of the feed, is recycled. The catalyst is regenerated.

A comparison shows that the conventional process operates at a temperature of 1023 – 1143K (750-870°C) and at a pressure of 31 – 37 atm whereas the new process operates at 600°C and 1 atm. Thus, this process operates at lower temperature and pressure than the conventional process. No by-product ethylene is produced, and the conversions of propane and selectivity to propylene are comparable to the conventional process. The reaction occurring in the new process is endothermic but requires less supply of heat compared to the conventional process. The new process is three to four times more economical compared to the conventional process (C & EN, June 2003, p.15). The information for this process is based on a new plant that has started its trial operations at Tarragona, Spain. Thus, this process is more realistic than laboratory scale processes.

Though this process does not use CO_2 as a raw material, it is more economical than the conventional process. The by-product H_2 obtained in the process can be used as a feedstock in other CO_2 hydrogenation processes. In conclusion, this process is selected for HYSYS simulation because it provides a source of propylene and hydrogen for the chemical complex.

B) Methanol

Methanol is also present in the list developed by Pacific Northwest National Laboratory (PNNL) with a potential energy savings of 37 trillion BTUs per year through improved catalysts (Pellegrino, 2000). The conventional processes for methanol include production from synthesis gas and also from natural gas. These processes will be briefly reviewed and fourteen new potential processes will be compared to the conventional process.

In the process using synthesis gas, the hydrocarbon feedstock is used to produce synthesis gas. The processing includes desulphurizing the hydrocarbon feedstock by passing over activated carbon or hot zinc oxide at 400ºC, mixing with high-pressure steam and passing it through a tubular reactor packed with nickel catalyst (Wells, 1999).

The synthesis gas thus produced is cooled to ambient temperature, and heat is recovered to generate the high-pressure steam required for the processing of hydrocarbon feedstock. Methanol is produced in a methyl converter in presence of Cu-Zn-Cr catalyst at 50 - 100 bar (49 – 99 atm) pressure and 250-260ºC temperature according to the following reaction (Wells, 1999).

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H^o = -90.5 \text{ kJ/mol}, \Delta G^o = -25 \text{ kJ/mol}.$$

The stoichiometric ratio of hydrogen to carbon in the synthesis gas is adjusted to 2:1. The yield of methanol obtained is 61%. The equipment for this process includes a reactor, separator and three distillation columns. The flow diagram representing this process is shown in Figure 3.2.

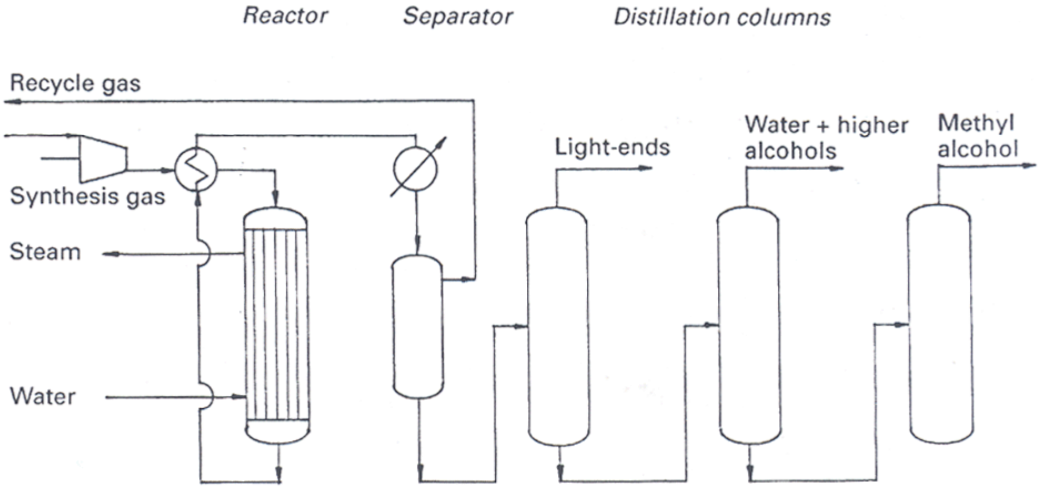


Figure 3.2. Methanol Production from Synthesis Gas, from Wells,1999.

In the process using natural gas, desulphurized natural gas is mixed with steam and is passed to the primary reformer. The exit gases along with preheated oxygen mixed with steam is fed into an oxygen-blown autothermal reformer (Wells, 1999). Synthesis gas with a ratio of hydrogen to carbon 2:1 is produced this way. The reactions involved are

$CH_4 + H_2O \rightarrow 3H_2 + CO$ Steam reforming
$CH_4 + \frac{1}{2} O_2 \rightarrow 2H_2 + CO$ Catalytic autothermal reforming

Methanol is produced in the presence of Cu-Zn-Cr catalyst at 50 - 100 bar (49 - 99 atm) pressure and 250-260ºC temperature. Depending on the composition of the synthesis gas produced, the following reactions are involved (Wells, 1999).

$CO + 2H_2 \rightarrow CH_3OH$ $\Delta H^o = -90.5$ kJ/mol, $\Delta G^o = -25$ kJ/mol. Yield 99%
$CO_2 + 3 H_2 \rightarrow CH_3OH + H_2O$ $\Delta H^o = -49$ kJ/mol, $\Delta G^o = 3$ kJ/mol. Yield 99%

The equipment for this process includes desulphurization tower, saturation tower, two reformers, converter and a separator cooler (Wells, 1999). The flow diagram representing this process is shown in Figure 3.3.

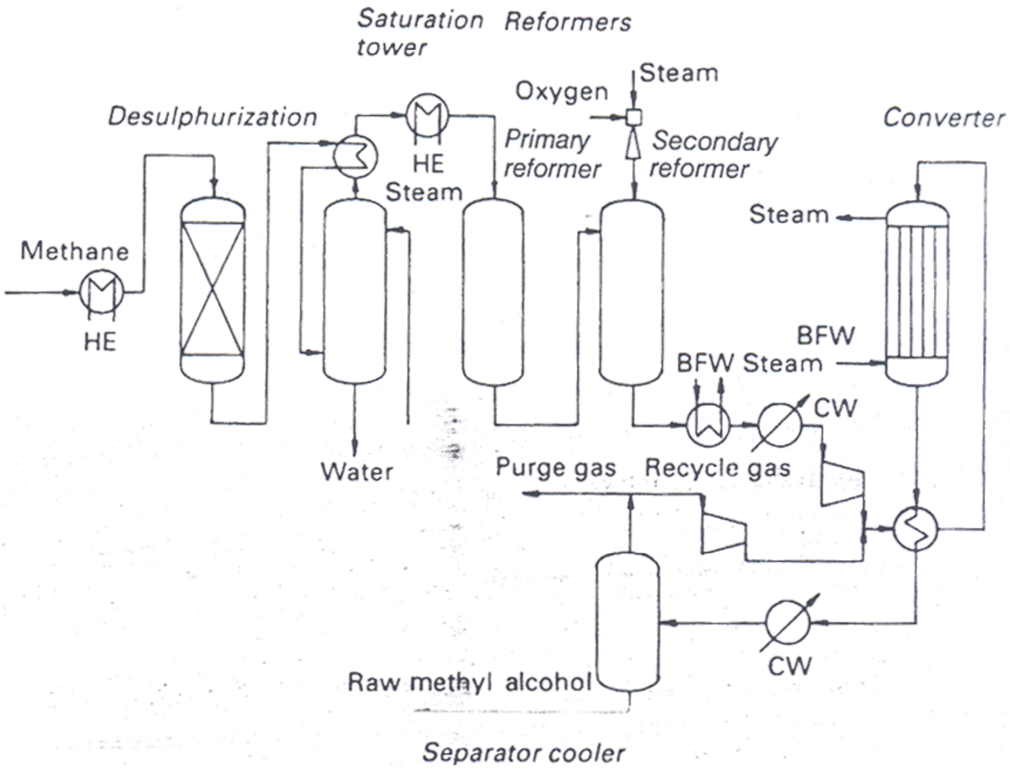


Figure 3.3. Methanol Production from Natural Gas, from Wells, 1999.

Inui, 2002, described four ways for the synthesis of methanol by CO_2 hydrogenation using multifunctional catalysts. A brief review of these four experimental studies is given below. The reaction involved for the hydrogenation of CO_2 is

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H^o = -49 \text{ kJ/mol}, \Delta G^o = 3 \text{ kJ/mol}.$$

The first experimental study involves carrying out CO_2 hydrogenation at 50 atm pressure and 523 K temperature. Cu-Zn-Cr-Al mixed oxide catalyst (CuO: ZnO: Cr_2O_3: Al_2O_3 = 25: 41.5: 1.2: 32.3 wt%) was used, and the mole ratio of hydrogen to carbon dioxide is 3:1. Conversion of CO_2 to methanol observed was 21.2% (Inui, 2002).

In the second study, CO_2 hydrogenation was carried out at a pressure of 80 atm and 523 K temperature using the same catalyst as before. The mole ratio of H_2 to CO_2 was 3:1. Conversion of CO_2 to methanol observed in this case is 28.5% (Inui, 2002).

In the third experimental study, CO_2 hydrogenation was carried out at a pressure of 80 atm and at a temperature of 563 K. Cu-Zn-Cr-Al mixed oxide catalyst (CuO: ZnO: Cr_2O_3: Al_2O_3 = 38.1: 29.4: 1.6: 13.1: 17.8 wt%, Pd 1 wt%) was used. The feed gas composition was 22% CO_2, 3% CO and 75% H_2. Conversion of CO_2 to methanol observed in this case was 25.1% (Inui, 2002).

The fourth experimental study involved carrying out the reaction at 563 K using the same feed gas composition as in the previous ones. A Four-component composite catalyst (CuO: ZnO: Cr_2O_3: Al_2O_3: Ga_2O_3: Pd = 37.7: 29.1: 1.6: 13.0: 17.6: 1 wt%) was used. The methanol selectivity and CO_2 conversion to methanol are 22% and 26.1% respectively (Inui, 2002).

These four new experimental studies are compared to the conventional processes. The temperatures and pressures of all the above four processes are in the same range as those of conventional processes. 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 (Cu-Zn-Cr-Al mixed oxide) used in these studies were not commercial catalysts (Cu-Zn-Cr mixed oxide) for methanol production. Consequently, these four studies are not selected for HYSYS simulation.

Nerlov and Chorkendorff, 1999, described a laboratory scale process for the synthesis of methanol from CO_2, CO, and H_2 over Cu(100) and Ni/Cu(100) catalysts. In this research using a Cu(100) catalyst, methanol was produced from a mixture of CO_2 and H_2 in a high-pressure cell at a temperature of 543 K and a pressure of 1.5 bar (1.5 atm). The composition of the feed gas was represented as partial pressures of the components. The partial pressures of CO_2 and H_2 for the maximum rate of formation of methanol were in the ranges of 450-750 mbar CO_2 and 1050-750 mbar H_2. The rate of formation of methanol was represented in terms of turnover frequency/site*s (TOF) and the observed value is 60 x 10^{-6} TOF/site*s. The author did not report the conversion of CO_2. The following reaction occurs in this study.

$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$ $\Delta H^o = -49$ kJ/mol, $\Delta G^o = 3$ kJ/mol.

The other articles that 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. The feed gas composition was 100 mbar CO, 30 mbar CO_2, and 1370 mbar H_2. The rate of formation of methanol observed was 60 x 10^{-6} TOF/site*s (Nerlov and Chorkendorff, 1999). The author did not report the conversion of CO_2. The reactions involved in this process are:

$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$ $\Delta H^o = -49$ kJ/mol, $\Delta G^o = 3$ kJ/mol
$CO + H_2O \rightarrow CO_2 + H_2$ $\Delta H^o = -41$ kJ/mol, $\Delta G^o = -29$ kJ/mol

The results in the above two articles are compared with the conventional process, which led to the following observations. The operating temperature in this new study is in the same range as that of the conventional process. But the operating pressure in the new study (1.5 bar) is less than that of conventional process (50-100 bar). The ratio of hydrogen to carbon is of the same range for both conventional process and the potentially new process using Cu(100) catalyst. However, the amount of H_2 required for the experimental study using Ni/Cu(100) catalyst is more when compared to the conventional process. Consequently, the potentially new process using Cu(100) catalyst is selected for HYSYS simulation, and the research using Ni/Cu(100) catalyst is not selected.

Omata, et al., 2002, described methanol synthesis from CO_2-containing synthesis gas. The reaction was carried out in a flow type fixed bed reactor at a temperature of

250°C and at a pressure of 10 atm. Cu-Mn catalysts supported on $ZnrO_2$ and TiO_2 were used in this research. The feed gas composition was $H_2/CO/CO_2/N_2$ = 60/30/5/5 and W/F = 4gh/mol. The conversion of CO_x to methanol was represented as STY (g-CH_3OH/kg-cat/h) where 1% CO_x conversion corresponds to STY 28 g-CH_3OH/kg-cat/h (Omata, et al., 2002). A conversion of STY 100 g-CH_3OH/kg-cat/h was observed at 50% Cu content of Cu-Mn-oxide catalyst. The reactions occurring in this process are

$$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H^o = -49\ kJ/mol,\ \Delta G^o = 3\ kJ/mol$$
$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H^o = -41\ kJ/mol,\ \Delta G^o = -29\ kJ/mol$$

In comparison, the experimental study operated at a pressure of 10 atm whereas the conventional process operates at 50-100 atm. The temperature at which both operate is same. The fuel gas used 30% CO and 5% CO_2. Thus, it is not a potential process that can consume excess high purity CO_2. The conversion of CO_2 to methanol is low in the experimental study when compared to the conventional process. The only advantage of this catalytic reaction is that it operates at a lower pressure than the conventional process. In conclusion, this research is not selected for HYSYS simulation.

Toyir, et al., 1998, described methanol synthesis from CO_2 hydrogenation. Raney Cu-Zr catalyst leached with aqueous solution of zincate (NaOH + ZnO) is used in this experimental study. The reaction was carried out in a flow reactor at a temperature of 523K and at a pressure of 5 MPa (50 atm). The ratio of hydrogen to carbon dioxide in the feed was 3:1 and the space velocity was 18000 h^{-1}. The main products of the reaction were methanol, water, and carbon monoxide. The methanol synthesis activity observed was 850 g-CH_3OH/l-cat-h (Toyir, et al., 1998). The authors reported that the Raney Cu-Zr catalyst developed in this research was significantly more active than a commercial catalyst. The reactions involved in this study are:

$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$ $\Delta H^o = -49$ kJ/mol, $\Delta G^o = 3$ kJ/mol
$CO_2 + H_2 \rightarrow CO + H_2O$ $\Delta H^o = 41$ kJ/mol, $\Delta G^o = 29$ kJ/mol

The temperature and pressure in this study are in the same range as that of the conventional process. The reactions are promising with their Gibbs free energies slightly above zero. The author compared the performance of this catalyst to that of a commercial $Cu/ZnO/Al_2O_3$ catalyst. The catalyst developed exhibited a specific activity of 41.4 mg-CH_3OH/m^2-cat-h whereas the commercial catalyst exhibited a specific activity of 17.1 mg-CH_3OH/m^2-cat-h. Thus, the new Raney Cu-Zr catalyst developed was significantly more active than a commercial catalyst (Toyir et al., 1998). Carbon monoxide is also obtained as a by-product. The ratio of hydrogen to carbon dioxide in the new study is 3:1 whereas the ratio of hydrogen to carbon in conventional process is 2:1. Thus this study required more H_2 than the conventional process. In conclusion, the catalyst exhibited better performance than a commercial catalyst, as discussed above. Therefore, this potentially new process is selected for HYSYS simulation.

Sahibzada, et al., 1998, described a laboratory process for the synthesis of methanol from CO_2 and H_2 over Pd promoted $Cu/ZnO/Al_2O_3$ catalysts. The reaction was carried in an internal recycle reactor (300 cm^3 volume, 100cm^3 catalyst basket) at a temperature and pressure of 250°C and 5 MPa (50 atm) respectively. The ratio of hydrogen to carbon dioxide in the feed gas was 4:1. The selectivity to methanol observed was 65%, and the rate of methanol production was 0.45 mol/h-g_{cu}. The catalyst exhibited a 10% loss of activity for every 40 hours of operation (Sahibzada, et al., 1998). The main products of this laboratory process were methanol, water and CO with CO being formed from reverse water-gas shift reaction. The reactions involved in this process are:

$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O$ $\Delta H^o = -49$ kJ/mol, $\Delta G^o = 3$ kJ/mol

$CO_2 + H_2 \rightarrow CO + H_2O$ $\Delta H^o = 41$ kJ/mol, $\Delta G^o = 29$ kJ/mol

A comparison of this laboratory process is made to the conventional process. The temperature and pressure of the new process are in the same range as that of the conventional process. The two reactions are feasible as their Gibbs free energies are 3 kJ/mol and 29 kJ/mol respectively. However, the catalyst exhibited a 10% loss of activity for every 40 hours. Also, the ratio of hydrogen to carbon dioxide is 4:1, which is twice that is needed in the conventional process. The author did not report the conversion of CO_2 to methanol. In conclusion, this laboratory process is not selected for HYSYS simulation.

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. A multicomponent catalyst ($Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3$) prepared by a conventional co-precipitation method was used. The reaction was carried out at 523 K and 5 MPa (50 atm). The feed gas composition was $H_2/CO_2 = 3/1$ and the space velocity was 10000 h^{-1}. The reactions occurring in the process are

$CO_2 + 3 H_2 \rightarrow CH_3OH + H_2O$ $\Delta H^o = -49$ kJ/mol, $\Delta G^o = 3$ kJ/mol
$CO_2 + H_2 \rightarrow CO + H_2O$ $\Delta H^o = 41$ kJ/mol, $\Delta G^o = 29$ kJ/mol
$CO + 2H_2 \rightarrow CH_3OH$ $\Delta H^o = -90.5$ kJ/mol, $\Delta G^o = -25$ kJ/mol

The mixture of carbon dioxide and hydrogen supplied from gas cylinders was 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. The mixture of methanol and water was taken out and stored in a container (Ushikoshi et al., 1998).

The rate of production of methanol was represented by space-time yield of methanol and the observed production rate was 700 g-CH_3OH/l-cat-h. The purity of the methanol synthesized was 99.9% (Ushikoshi, et al., 1998).

The pilot plant was carried out with recycling equipment for unreacted gases since the conversion of CO_2 to methanol at reaction equilibrium is low under ordinary reaction conditions. The conversion of CO_2 at 523 K and 5 MPa (50 atm) was 17%. Thus, unreacted gases and gaseous products like CO were recycled back to the reactor (Ushikoshi, et al., 1998).

The author compared the catalyst performance with a commercial $Cu/ZnO/Al_2O_3$ catalyst. The new catalyst exhibited an 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. Thus, the new catalyst used in the pilot plant exhibited higher activity than a commercial catalyst ($Cu/ZnO/Al_2O_3$). The catalyst was stable for a long period in continuous methanol synthesis. However, the author did not report an exact time period for catalyst deactivation (Ushikoshi, et al., 1998).

Comparing the pilot plant results to the conventional process, the following observations were made. The operating temperature and pressure were in the same range as that of the conventional process. The reactions are feasible as their Gibbs free energies are slightly above zero. The catalyst has superior characteristics than many other catalysts including a commercial one. The purity of methanol produced was 99.9%, and yield of methanol was 700 g-CH_3OH/l-cat-h, and is higher than that of a commercial catalyst as discussed earlier (Ushikoshi, et al., 1998). Consequently, this potentially new process is selected for HYSYS simulation.

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. The conversion of CO_2 and the selectivity of methanol were 23.4% and 5.2%. The results show that the catalyst used was effective for the formation of C_{2+} hydrocarbons. The catalyst also resulted in the suppression of CO formation (Nomura, et al., 1998).

A comparison between the potentially new process and the conventional process led to the following observations. This research was carried out at 553 K whereas the conventional process is conducted at 523 K. The experimental study was operated at a pressure of 10 atm whereas the conventional process operates at 50-100 atm pressure. Therefore, the experimental study was carried out at a pressure that is less than that of the conventional process. This experimental study required about twice the hydrogen needed in the conventional process. The conversion of carbon dioxide and selectivity to methanol was low, and the catalyst was effective for the formation of C_{2+} hydrocarbons than the formation of methanol. The author did not report the reaction mechanism occurring in this process. In conclusion, this experimental study is not selected for HYSYS simulation.

Jun, et al., 1998, described hydrogenation of CO_2 over hybrid catalyst of Cu/ZnO/Cr_2O_3 and CuNaY zeolite for the synthesis of methanol and dimethyl ether (oxygenates). The feed gas composition was $H_2/CO_2 = 3/1$. The reaction was carried out in a fixed bed micro-reactor at 523 K, 30 kg/cm^2 (30 atm) pressure, 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% (Jun, et al., 1998). The reactions occurring in this process are:

$CO_2 + H_2 \rightarrow CO + H_2O$ $\Delta H^o = 41$ kJ/mol, $\Delta G^o = 29$ kJ/mol
$CO + 2H_2 \rightarrow CH_3OH$ $\Delta H^o = -90.5$ kJ/mol, $\Delta G^o = -25$ kJ/mol
$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$ $\Delta H^o = -24$ kJ/mol, $\Delta G^o = -17$ kJ/mol

This laboratory study is compared to the conventional process. The research operates at the same temperature as that of the conventional process. This study operated at 30 atm pressure whereas the conventional process operates at 50 – 100 atm. The three reactions occurring in this study are thermodynamically feasible as their Gibbs free energies are 29, -25, -17 kJ/mol respectively. Dimethtl ether 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. In conclusion, the potentially new process is selected for HYSYS simulation.

Mabuse, et al., 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%). The ratio of hydrogen to carbon dioxide in the feed gas was 3:1. The reaction was carried out in a liquid-phase continuous reactor at a temperature and pressure of 523 K and 15 MPa (150 atm). The recycle rate of the solvent was 100 lit-solvent/lit-cat/hr and the observed rate of formation of methanol was 650 g-CH_3OH/kg-cat-hr. The hydrogenation reaction occurring in the study is given below.

$CO_2 + 3 H_2 \rightarrow CH_3OH + H_2O$ $\Delta H^o = -49$ kJ/mol, $\Delta G^o = 3$ kJ/mol

The temperature at which this reactor operates is in the same range as that of conventional process. The operating pressure for the reactor is 15 MPa (150 atm) but it is 50-100 bar (50- 100 atm) in the conventional process. Thus this reactor operates at about

1.5-3 times the pressure of the conventional process. In conclusion, the above study is not selected for HYSYS simulation as it operates at considerable higher pressure than the conventional process.

Fukui, et al., 1998, described a new preparation method for Cu/ZnO catalysts for methanol synthesis from hydrogenation of carbon dioxide. The catalyst was prepared by mechanical alloying method where as the conventional catalyst is prepared by co-precipitation methods. The catalyst used in this research, which was milled for 120 hours, demonstrated a catalytic activity of about 1.5 times higher than that over conventional co-precipitated Cu/ZnO catalyst (Fukui et al., 1998).

The reaction was carried out in a flow type fixed bed reactor at 250°C and 5 MPa (50 atm). The feed gas composition was $H_2/CO_2 = 3:1$, with a space velocity of $26,000h^{-1}$. The observed rate of synthesis of methanol was 350 g/l-cat-h (Fukui, et al., 1998). The reaction occurring in the study is given below.

$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H^o = -49$ kJ/mol, $\Delta G^o = 3$ kJ/mol

The operating temperature and pressure are in the same range as that of the conventional process. Although the catalyst exhibited an activity of about 1.5 times higher to that of a conventional catalyst, the process is very similar to an earlier process described by Ushikoshi, et al., 1998. The methanol production rate was 350 g/l-cat-h, but it was 600 g/l-cat-h in the study described by Ushikoshi, et al., 1998. Since this study by Ushikoshi et al., 1998 has been already selected for simulation it is not worth selecting this study. Consequently, this study is not selected for HYSYS simulation.

Bonivardi, et al., 1998, described another process where methanol was produced from CO_2 hydrogenation over Ca promoted Pd/SiO_2 catalyst. The composition of the feed gas was H_2/CO_2 = 3:1. The reaction was carried out in a copper-plated differential microreactor at 523 K, 3 MPa (30 atm), and with a space velocity of 10000 h^{-1}. The observed rate of synthesis of methanol was 50 x 10^{-8} mol/gPd-s. The selectivity to methanol was more than 95% (Bonivardi, et al., 1998).

The author suggests 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. This suggests that large recycle ratios would have to be employed to maintain the selectivity to methanol in a commercial process (Bonivardi, et al., 1998). The reactions occurring in this study are:

$CO_2 + H_2 \rightarrow CO + H_2O$ $\Delta H^o = 41$ kJ/mol, $\Delta G^o = 29$ kJ/mol
$CO + 2H_2 \rightarrow CH_3OH$ $\Delta H^o = -90.5$ kJ/mol, $\Delta G^o = -25$ kJ/mol

The above study is compared to the conventional process. The operating temperature of this study is in the same range as that of the conventional process. This study was conducted at 30 atm pressure where as the conventional process operates at 50-100 atm pressure. Thus, this potential process would operate at a pressure less than the conventional process. The first reaction is endothermic, and the second reaction is exothermic. Both the reactions are thermodynamically feasible because of their low Gibbs free energies. The selectivity to methanol in this study is comparable to that of the conventional process. In conclusion, this potentially new process is selected for HYSYS simulation.

Hara, et al., 1998, described a laboratory process for the synthesis of gasoline from carbon dioxide via methanol as an intermediate. The feed gas was a CO_2 rich gas with composition $CO_2/CO/H_2$ = 22/3/75. The catalyst used was 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). The reaction was carried out in a pressurized reactor at 270°C, 80 atm, and at a space velocity of 18800 h^{-1}. The conversion of CO_2 to methanol was 22%.

The products from the reactor were fed into a second reactor where methanol was converted to gasoline at 320°C and 15 atm (Hara, et al., 1998). The author did not mention the reaction mechanism for the production of gasoline.

The conventional process operates at 250°C whereas this laboratory process operates at 270°C. The conventional process operates at 50-100 atm pressure where as the new process operates at 80 atm pressure. Therefore, this study fails to provide any advantage in the operating conditions compared to the conventional process. Also, the reaction mechanism for the production of gasoline from methanol is not defined. In conclusion, this study is not selected for HYSYS simulation.

Bill, et al., 1998, described two different methods for the production of methanol from CO_2 hydrogenation. The first one describes methanol production from CO_2 and H_2 in a conventional tubular packed-bed reactor filled with copper based catalyst ($CuO/ZnO/Al_2O_3$). The feed gas composition was $H_2/CO_2 = 3:1$. The reaction was carried out at 220°C, 20 bar (20 atm), and with a space velocity of 4500 h^{-1}. The methanol yield and selectivity observed were 7.1% per single pass and 43.8% respectively. Other major products were carbon monoxide and water due to reverse water-gas shift reaction (Bill, et al., 1998).

The second experimental study uses a dielectric-barrier discharge (DBD) with the aid of a catalyst inside the discharge space. In this case, the operating temperature was lowered to 100°C and the methanol yield was increased by a factor of ten (Bill et al., 1998).

Both the above new methods described by Bill, et al., 1998, are compared to the conventional process. The first method operates at a temperature and pressure less than the conventional process. But, the yield and selectivity were 7.1% per single pass and 43.8% respectively, which were low when compared to the conventional process. The second method uses a dielectric-barrier discharge, and could not be considered for HYSYS simulation. In conclusion, both the methods are not selected for HYSYS simulation.

Hirano, et al., 1998, described a laboratory process for methanol production from CO_2 and H_2 using $CuO\text{-}ZnO\text{-}Al_2O_3$ catalyst (Al_2O_3 5 wt%). The reaction was carried out in a microreactor at 513-521 K, 9 MPa (90 atm), with a space velocity of 5000 h^{-1}, and with a feed gas composition of $H_2/CO_2 = 3/1$. The recycle ratio used in this laboratory process was 4 m^3N/m^3N. The recycling test conducted for 3000 hours demonstrated that about 95% of supplied carbon dioxide was converted into methanol (Hirano, et al., 1998). The methanol yield was 22%, which was close to the equilibrium methanol yield of 25%. The catalyst performance was compared to two kinds of commercial $CuO\text{-}ZnO\text{-}Al_2O_3$ catalysts. The new catalyst exhibited nearly twice the yield of methanol yield as exhibited by the commercial catalysts in the temperature range of 513-521 K (Hirano, et al., 1998).

Comparison of the above potentially new process to the conventional process led to the following observations. The operating temperature of the laboratory process is in the same range as that of the conventional process, and it operates at 90 atm whereas the conventional process operates at 50-100 atm. Therefore, this potentially new process might operate at a higher pressure than that of the conventional process. This reactor operates at a higher pressure than the rest of the potentially new processes already selected for simulations. The catalyst demonstrated nearly twice the activity as that of a commercial catalyst in the temperature range of 513-521 K (Hirano, et al., 1998). In conclusion, this study is not selected for HYSYS simulation as it operates at a higher pressure.

C) Ethanol

The first commercial process used for ethyl alcohol production was the indirect catalytic hydration of ethylene. It had several disadvantages such as handling large volumes of dilute sulfuric acid, energy required for its concentration, and corrosion caused by the acid (Wells, 1999). The current industrial processes for the manufacture of ethyl alcohol are direct catalytic hydration of ethylene and carbonylation of methyl alcohol (Wells, 1999). A brief description of these two conventional processes is presented below.

In the direct hydration of ethylene, the reaction is conducted in a reactor containing a fixed-bed catalyst consisting of 77% phosphoric acid absorbed onto a carrier such as silica gel. The operating temperature and pressure are in the range of 230-300°C and 60-80 bar (60-80 atm) respectively. Ethyl alcohol is produced according to the following reaction (Wells, 1999).

$$CH_2 = CH_2 + H_2O \rightarrow C_2H_5OH \qquad \Delta H^o = -45.5 \text{ kJ/mol}, \Delta G^o = -8 \text{ kJ/mol}$$

The conversion of ethylene to ethanol is about 4% per pass. Large recycle volume of unconverted ethylene is usually employed, and this cyclic process eventually gives a net yield of 97% (Speight, 2002). The reaction is exothermic, and the excess heat is used to raise the temperature of the incoming feed (Wells, 1999). The flow diagram representing this process is shown in Figure 3.4.

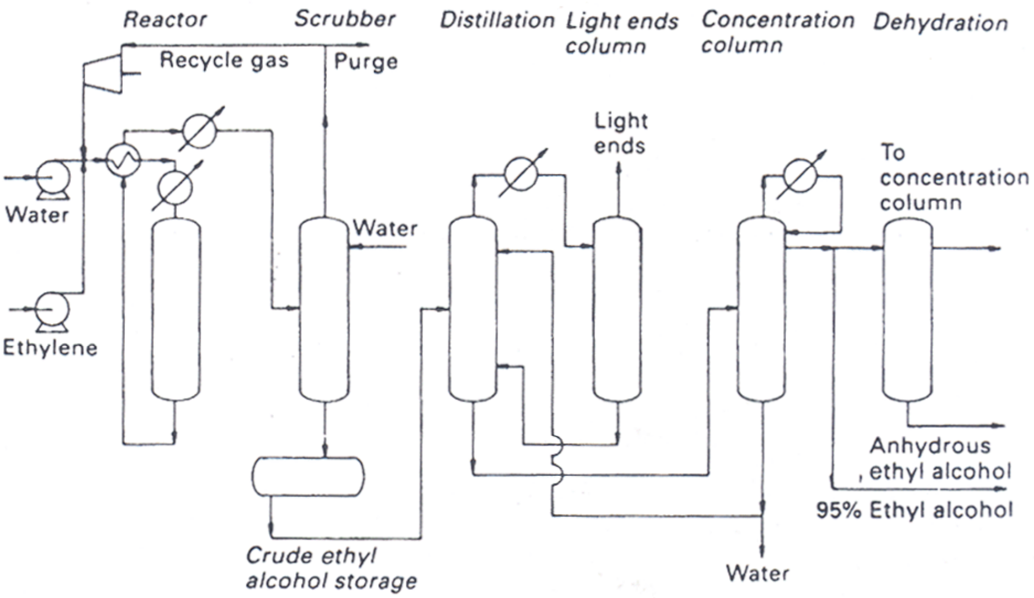


Figure 3.4. Ethanol Production from Direct Hydration of Ethylene, from Wells, 1999.

The gaseous mixture leaving the reactor is cooled and washed with dilute alkali solution to neutralize any vaporized phosphoric acid that may be entrained with the gases (Wells, 1999). Crude ethyl alcohol is sent to a purification section where a product of 95% (volume) ethyl alcohol is formed (Speight, 2002). The dehydration section produces high-purity ethyl alcohol free of water. For many industrial uses, the 95% purity product from the purification section is sufficient (Speight, 2002).

Important factors affecting the conversion of ethylene to ethanol include temperature, pressure, water/ethylene ratio, recycle of unreacted ethylene, and the purity of ethylene (Speight, 2002). The molar ratio of ethylene to water generally used is 1:0.3-0.8 (Wells, 1999).

Dehydration of ethyl alcohol into diethyl ether is a side reaction where about 2% of diethyl ether is produced as by-product. It is usually recovered and sold, but it can be recycled to the reactor for conversion to ethyl alcohol. The yield of ethanol is 94-95% if ether is recovered and 96-97% if ether is recycled (Wells, 1999). Diethyl ether is formed according to the following reaction (Speight, 2002).

$2C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O \quad \Delta H^o = -24$ kJ/mol, $\Delta G^o = -15$ kJ/mol

The catalyst life is about three years. The equipment needed for this process include a reactor, scrubber, three distillation columns, and a dehydration tower (Wells, 1999).

In the carbonylation of methyl alcohol, three-stage are used. In the first stage methyl alcohol, produced from synthesis gas, is combined with carbon monoxide in the liquid phase in the presence of carbonyls of non-noble metals such as tungsten, molybdenum or chromium. The acetic acid formed is esterified with methyl alcohol to methylacetate in a tower reactor (Wells, 1999). The flow diagram representing this process is shown in Figure 3.5. The overall reaction occurring in the process is given below (Wells, 1999).

$CH_3OH + CO + 2H_2 \rightarrow C_2H_5OH + H_2O \quad \Delta H^o = -165$ kJ/mol, $\Delta G^o = -97$ kJ/mol

The reaction mixture is distilled and overheads are recycled to the reactor, while the crude acetic acid stream is dried before passing to the ethyl alcohol unit (Wells, 1999). The methyl acetate is dried and hydrolyzed to ethyl alcohol and methyl alcohol (Wells, 1999).

The process has been modified so that the methyl acetate formed is carbonylated to acetic anhydride, which is then reacted with methyl alcohol and ethyl alcohol to yield their respective acetates. These are separated by distillation, and ethyl acetate is hydrolyzed in the presence of sulfuric acid to ethyl alcohol. The methyl acetate is carbonylated to ethyl alcohol.

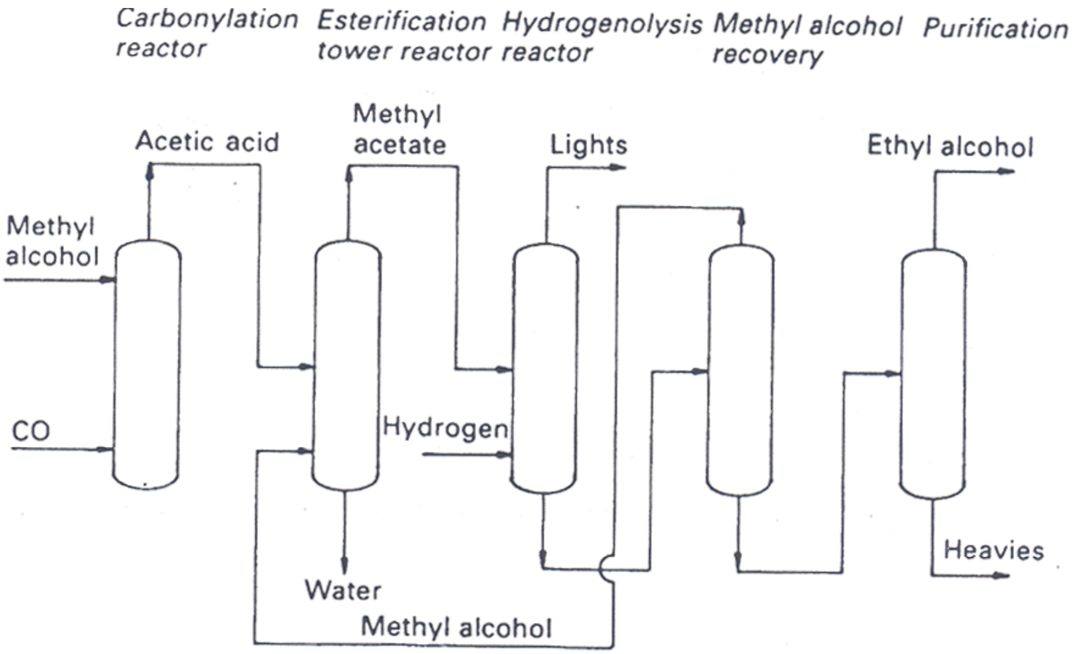


Figure 3.5. Ethanol Production from Carbonylation of Methyl Alcohol, from Wells, 1999.

The potentially new processes, which use CO_2 for the production of ethanol, are described below. These experimental studies will be compared with the existing commercial processes, and the candidate processes will be selected for HYSYS simulation.

Inui, 2002 reviewed two experimental studies described earlier by different authors for synthesis of ethyl alcohol from the hydrogenation of carbon dioxide. In the first study, CO_2 hydrogenation was carried out at a temperature and pressure of 573 K (300°C) and 69 atm respectively. The catalyst was Rh-Li-Fe/SiO_2. The composition of the feed gas was $H_2/CO_2 = 3/1$. The conversion of carbon dioxide to ethanol was 10.5%, and the selectivity to ethanol was 10.5% (Inui, 2002).

In the second experimental study, the hydrogenation reaction was carried at a temperature range of 513-533K (240-260°C) and at a pressure of 49 atm. The catalyst was Cu-Zn-Fe-K. The composition of the feed gas was $H_2/CO_2 = 3/1$. The conversion of carbon dioxide to ethanol was 21.2%, and the selectivity to ethanol was 21.2% (Inui, 2002). The following reaction occurs in both the experimental studies.

$2CO_2 + 6H_2 \rightarrow C_2H_5OH + 3H_2O \qquad \Delta H^o = -173$ kJ/mol, $\Delta G^o = -65$ kJ/mol

The above two methods are compared to the conventional process. The conventional process operates at a temperature range of 230-300°C and at a pressure of 60-80 atm. Thus, the temperature and pressure of the first potential process, which operates at 300°C and 69 atm, are in the same range as that of conventional process. The conversion of carbon dioxide is moderate (10.5%) although higher than the conversion of ethylene in conventional process (4%). Based on heat of reactions and Gibbs free energies, the reaction in this study is more exothermic and thermodynamically feasible than the conventional process.

The second potential process operates at a pressure of 49 atm, which is less than that of the conventional process (60-80 atm). The conversion obtained in this potential process (21.2%) is more than that of the conventional process (4%) and the other new potential process (10.5%) discussed above. Based on heat of reactions and Gibbs free energies, the reaction in this potential process is more exothermic and thermodynamically feasible than the conventional process.

In conclusion, the second potential process has more advantages than the first potential process when both were compared to the conventional process. Consequently, the second study is selected for HYSYS simulation whereas the first study is not selected.

Inui, 2002 described three other experimental studies for synthesizing ethanol from CO_2 and H_2. These three experimental studies are briefly discussed below. The first study was carried out at 583 K (310°C) and 80 atm. The composition of the feed gas was

H_2/CO_2 = 3/1 and the space velocity was 20,000 h^{-1}. The catalyst used was Fe-Cu-Zn-Al-K. The conversion of carbon dioxide and the selectivity to ethanol was 28.5% each (Inui, 2002).

The second study was carried out at 623 K (350°C) and 80 atm. The composition of the feed gas was H_2/CO_2 = 3/1 and the space velocity was 70,000 h^{-1}. (Rh/MFI-silicate)-(Fe-Cu-Zn-Al-K) catalyst packed in series was used in the reactor. The conversion of carbon dioxide and the selectivity to ethanol was 12.8% each (Inui, 2002).

The third experimental study was carried out at 603 K (330°C) and 80 atm. The composition of the feed gas was H_2/CO_2 = 3/1 and the space velocity was 50,000 h^{-1}. (Fe-Cu-Al-K) (Cu-Zn-Al-K.Ga.Pd) physically mixed catalyst was used. The conversion of carbon dioxide and the selectivity to ethanol was 25.1% each (Inui, 2002). The following reaction occurs in all the three studies.

$$2CO_2 + 6H_2 \rightarrow C_2H_5OH + 3H_2O \qquad \Delta H^o = -173 \text{ kJ/mol}, \Delta G^o = -65 \text{ kJ/mol}$$

The above three experimental studies were compared to the conventional process, and the following observations were made. All the three studies operate at a slightly higher temperature than that of the conventional process. The operating pressures for all the three studies are in the same range as that of conventional process. Based on the heat of reactions and Gibbs free energies, the reaction in the potentially new processes is more exothermic and thermodynamically feasible than the conventional process. The conversions observed in all the three new processes are higher than the conventional process.

In conclusion, the new experimental studies operate at a higher temperature than the conventional process and do not provide any pressure advantage than the conventional process. Therefore, all the three processes are not selected for HYSYS simulation.

Kusama, et al., 1998 described a laboratory process for ethanol synthesis through hydrogenation of carbon dioxide. The reaction was carried out in a pressurized fixed bed, flow-type micro reactor over 5 wt% Rh/SiO_2 catalyst. The operating temperature and pressure were 533K (260°C) and 5 MPa (50 atm) respectively. The feed gas composition was H_2:CO_2 = 3:1 and the flow rate was 100 cm^3/min. The selectivity to ethanol observed was 2% (Kusama, et al., 1998). The following reaction occurs in this study.

$$2CO_2 + 6H_2 \rightarrow C_2H_5OH + 3H_2O \qquad \Delta H^o = -173 \text{ kJ/mol}, \Delta G^o = -65 \text{ kJ/mol}$$

The above laboratory process is compared to the existing commercial process. The operating temperature is in the same range as that of the conventional process. The new process operates at a slightly lesser pressure (50 atm) than the conventional process (60-80atm). The selectivity to ethanol observed in the study is less when compared to the other new potential processes that were selected for HYSYS simulation. In conclusion, this new laboratory process is not selected for HYSYS simulation.

Bando, et al., 1998, described another laboratory process for the hydrogenation of carbon dioxide over Rh ion exchanged zeolite catalysts. Li-impregnated RhY catalyst (Li/RhY = 1-15, Rh concentration = 5 wt%) was used. The reaction was carried out in a fixed bed flow reactor at 523 K (250°C) and 3 MPa (30 atm). The feed gas contains hydrogen and carbon dioxide with a composition of 3:1, along with 1.8% CO. Main products of the reaction include methane, carbon monoxide, and ethyl alcohol. About 7% conversion of carbon dioxide and 16% selectivity to ethanol was observed. The selectivities to methane and carbon monoxide were 40% and 38% respectively (Bando, et al., 1998). The author did not specify the reaction mechanism for the formation of these products.

A comparison is made between the above new laboratory process and the conventional process. Though the operating temperature is in the same range as the conventional process, the new study operates at about half the pressure of the conventional process. The conversion of CO_2, and selectivity to ethanol were mentioned earlier, and they are reasonable within the specified pressure range. By-products such as methane and carbon monoxide are also produced. In conclusion, the potentially new process is selected for HYSYS simulation.

Yamamoto and Inui, 1998, described a method for the synthesis of ethanol over Fe, Cu-based novel catalysts. The catalyst used was a combination of Cu-Zn-Al-K mixed oxide catalyst and Fe-Cu-Al-K mixed oxide catalyst. Pd and Ga were added to modify the catalyst. The reaction was operated at a temperature of 330°C and at a pressure of 80 atm. The feed gas composition was $H_2/CO_2 = 3/1$ and the space velocity was 20,000 h^{-1}.

About 54.5% CO_2 conversion to products was observed. The reaction products include ethyl alcohol, methanol, hydrocarbons, and carbon monoxide. The selectivity to ethanol was 17% and that of hydrocarbons was 64.5%. Specific conversion of CO_2 to ethanol was about 5% and the space-time yield of ethanol was 476 g/l.h (Yamamoto and Inui, 1998). The authors have not mentioned the reaction mechanism and the specification of hydrocarbons produced.

Based on the comparison with the conventional process, the potentially new process operates at a higher temperature than the conventional process. The operating pressure is 80 atm, which is also higher compared to the other selected new processes.

Though the conversion of CO_2 is higher, its specific conversion to ethanol is low. The reaction mechanism occurring was not mentioned, and specifications of the formed hydrocarbons were unclear. In conclusion, this process is not selected for HYSYS simulation.

Higuchi, et al., 1998, performed an experimental study for the durability of catalysts in ethanol synthesis by CO_2 hydrogenation. K/Cu-Zn-Fe-Cr oxide catalyst exhibited a long catalytic life because of its slow segregation rate. The hydrogenation reaction was carried out in a conventional flow reactor at 300°C and 7 MPa (70 atm). A steady 35% conversion of CO_2 and 16% selectivity to ethanol was observed (Higuchi, et al., 1998). The following reaction occurs in the process.

$$2CO_2 + 6H_2 \rightarrow C_2H_5OH + 3H_2O \qquad \Delta H^o = -173 \text{ kJ/mol}, \Delta G^o = -65 \text{ kJ/mol}$$

This experimental study was compared to the conventional process, and the following observations were made. The operating temperature and pressure are in the same range as that of conventional process. The conversion of CO_2 and selectivity to ethanol are 35% and 16% respectively, which are reasonable. The conversion of ethylene to ethanol in conventional process was 4% per pass. Thus, this study has a higher conversion than the commercial process. The author also mentioned that the catalyst used in the study exhibited a long life without deactivation. In conclusion, this study is selected for HYSYS simulation.

Takagawa, et al., 1998, described hydrogenation of carbon dioxide for the synthesis of ethanol over K/Cu-Zn-Fe oxide catalyst. The reaction was operated at a temperature of 300°C and at a pressure of 7MPa (70 atm). The composition of feed gas was H_2/CO_2 =3/1. The catalyst gave an ethanol selectivity of 20% with a CO_2 conversion of 44%. However, the catalyst declined quickly during the reaction (Takagawa, et al., 1998). The other products formed along with ethanol include carbon monoxide, methanol, oxygenates, and hydrocarbons.

A comparison is made between this study and the conventional process. The operating temperature and pressure of this study were in the same range as that of the conventional process. Thus, this study does not provide any advantage over the conventional process in this point-of-view. Though the catalyst exhibited good selectivity to ethanol with a high CO_2 conversion of 44%, its activity declined quickly during the reaction (Takagawa, et al., 1998). Thus, this catalyst could not be treated as a commercial one. Consequently, this study is not selected for HYSYS simulation.

Izumi, et al., 1998, described the synthesis of ethanol from carbon dioxide and hydrogen over $[Rh_{10}Se]/TiO_2$ catalyst. The reaction temperature and pressure were 523K (250°C) and 47 kPa (0.47 atm) respectively. The reaction was carried out in a closed circulation system with a dead volume, 210 cm^3. The feed gas consists of H_2 and CO_2 with a ratio of 2:1. The rate and selectivity of ethanol has strong dependence on heating temperature in vacuum (evacuation temperature) and the evacuation temperature corresponding to maximum selectivity and conversion was 623 K (350°C). The catalyst exhibited high activity with 83% ethanol selectivity and 80% CO_2 conversion.

Methane and carbon monoxide were obtained as by-products. The rates of ethanol synthesis and by-products were $1.9/10^{-3}$ $molh^{-1}g_{cat}$-^{1} and 0.4/10-3 $molh^{-1}g_{cat}^{-1}$ respectively (Izumi, et al., 1998). The catalyst demonstrated that ethanol was not formed via CO. The reaction path for the formation of ethanol is CH_x (a) + CO_y (a) → acetate (a) → ethanol (Izumi, et al., 1998).

Based on the comparison made between this study and the conventional process, the following observations were made. The operating temperature of this study is in the same range as that of the conventional process. The conventional process operates at a pressure of 60-80 atm whereas this study operates at about 0.47 atm. This research has an advantage over the conventional process as it a operating at a very low pressure (0.47 atm). The values of CO_2 conversion and ethanol selectivity are 80% and 83% respectively. The author mentioned that the catalyst has high activity but did not compare with the existing commercial catalysts. The ratio of H_2 to CO_2 required is 2:1. Thus, this study requires less hydrogen than many other processes where ethanol is produced by CO_2 hydrogenation. However, the reaction mechanism was unclear. Thus, this study cannot be simulated using HYSYS for this reason. Consequently, this potentially new process is not selected for HYSYS simulation.

D) Dimethyl Ether

Dimethyl ether (DME) is used primarily as a propellant. DME is produced commercially by catalytic dehydration of methanol over an amorphous alumina catalyst treated with 10.2% silica (Turton, et al., 1998). Dimethyl ether is produced according to the following reaction.

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H^o = -24 \text{ kJ/mol}, \Delta G^o = -17 \text{ kJ/mol}$$

Fresh methanol mixed with recycled reactant is vaporized and sent to a fixed-bed reactor. The dehydration reaction occurs at a temperature of 250-368ºC and a pressure of about 15 bar. The single-pass conversion of methanol is about 80% (Turton, et al., 1998). The process uses two distillation columns. The reactor effluent is cooled and sent to the first distillation column where DME is separated and collected as an overhead product.

Water and unreacted methanol are separated in the second distillation column. Unreacted methanol is recycled back, and water is sent to waste treatment to remove trace amounts of organic compounds (Turton, et al., 1998).

Three potentially new processes that use CO_2 as a raw material for the production of dimethyl ether (DME) will be discussed. Another process, which natural gas is used as a feedstock for the direct synthesis of DME will be briefly described. Processes having more advantages over the conventional process will be selected for HYSYS simulation.

Jun, et al., 2002, described a potentially new process for the synthesis of dimethyl ether from CO_2 hydrogenation. The γ-Al_2O_3 modified with 1% silica was used as a catalyst. The commercial catalysts modified with B_2O_3, ZrO_2, or SiO_2 have lower surface area than the catalyst used here. The commercial catalyst has a BET surface area of 160.3 m^2/g and that of the new catalyst was 206.8 m^2/g (Jun, et al., 2002). The author also mentioned that the catalyst exhibited stable activity for over 100 h at 523 K. The catalyst also exhibited resistance to the water produced from CO_2 hydrogenation, and showed no signs of deactivation (Jun, et al., 2002). The following reactions occur in the reactor.

$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ $\Delta H^o = -49$ kJ/mol, $\Delta G^o = 3.5$ kJ/mol
$CO_2 + H_2 \rightarrow CO + H_2O$ $\Delta H^o = 41$ kJ/mol, $\Delta G^o = 29$ kJ/mol
$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$ $\Delta H^o = -24$ kJ/mol, $\Delta G^o = -17$ kJ/mol

The reaction was carried out in a fixed-bed reactor at 523 K (250°C). The author did not mention the total operating pressure. However, the partial pressure of methanol was mentioned to be 101.2 torr, from which the total pressure could be assumed based on stoichiometric ratios of the reacting components. In this manner, the total pressure was calculated to be 404.8 torr (0.53 atm). The conversion of methanol observed was 70% at 523 K (Jun, et al., 2002).

The study is compared to the conventional process. As discussed earlier, the new catalyst exhibited a better performance than the commercial catalysts. The reactions are thermodynamically feasible, based on their heats of reactions and Gibbs free energies. The conventional process operates at 250 – 368°C whereas this reactor operates at 250°C. Thus, this reactor might operate at a temperature below that of the conventional process. If the estimated total pressure in this study (0.53 atm) was justified, then this process operates at a very low pressure when compared to the conventional process (15 atm). The author did not report the conversion of CO_2 in this process. However, the conversion of methanol was reported to be 70%. The conversion of methanol in the conventional process is 80% (Turton et al., 1998). Thus, methanol conversions in both the processes are comparable to each other. In conclusion, this potentially new process is selected for HYSYS simulation.

Tao, et al., 2001, described a laboratory process for co production of methanol and dimethyl ether from CO_2 hydrogenation over a stable hybrid catalyst. The hybrid catalyst used was a mixture 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)). The overall reaction was carried out at 523 K and 3 MPa (30 atm). The catalyst lost 5% of its activity in 120 h, and exhibited no significant activity until 350 h. The total yield of dimethyl ether and methanol was higher than 26% with over 90% selectivity to dimethyl ether (Tao, et al., 2001). The following reactions occur in the reactor.

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H^o = -49 \text{ kJ/mol}, \Delta G^o = 3.5 \text{ kJ/mol}$$
$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H^o = -24 \text{ kJ/mol}, \Delta G^o = -17 \text{ kJ/mol}$$

The above study is compared to the conventional process. The conventional process operates at a pressure of 15 bar (15 atm) whereas the study operates at 3 MPa (30 atm). Thus, this study operates at twice the pressure of the conventional process. The conventional process operates at 250-368 °C whereas the study operates at 523 K (250°C). The heats of reactions are negative indicating that the reactions are exothermic. The negative value and low positive values of Gibbs free energies indicate that the reactions are thermodynamically feasible. In conclusion, since the experimental study operates at twice the operating pressure of the conventional process, it is not selected for HYSYS simulation.

Jun, et al., 1998, described a process for production of methanol and dimethyl ether through CO_2 hydrogenation over a hybrid catalyst of $Cu/ZnO/Cr_2O_3$ and CuNaY zeolite. This method is earlier described as a new potential process for methanol using CO_2 as a raw material. This method was already selected for HYSYS simulation, and therefore need not be compared again with the conventional process.

Romani, et al., 2000, described a large-scale process for the production of dimethyl ether from natural gas. This process was developed by Haldor Topsoe, and does not require the production and purification of methanol. The process has three stages. The first stage is the synthesis gas preparation by auto thermal reforming. It is similar to a conventional reforming section, with the exception of low steam/carbon ratio of 0.6 (Romani, et al., 2000).

The second stage involves combined synthesis of methanol and dimethyl ether (DME). The reaction from synthesis gas to DME is a sequential reaction, involving methanol as an intermediate. The reaction occurs in an adiabatic fixed bed reactor loaded with proprietary Topsoe dual-function catalyst. The catalyst has been tested in excess of 30,000 hours in a DME process demonstration unit (Romani, et al., 2000). The author did not mention any detailed process information such as the operating conditions, reactant conversions, and product yields.

The third stage involves product separation and purification. The lower the demand for product purity, the lower the investment and energy consumption. Substantial savings were achieved by producing fuel grade DME, i.e., DME containing minor amounts of methanol and water (Romani, et al., 2000).

The author claimed that this process is more economical than the traditional fixed bed catalytic dehydration of methanol. However, the author did not mention the process details such as process operating conditions. The process uses natural gas as a raw material. Thus, this process cannot consume the excess high purity carbon dioxide available in the lower Mississippi River Corridor. In conclusion, this process is not selected for HYSYS simulation.

E) Formic Acid

Over half of formic acid production worldwide comes from hydrolysis of methyl formate. The low raw material cost makes this process the main route of choice for formic acid production (Wells, 1999). Formic acid is also produced along with sodium sulfate from sodium formate by acidolysis. However, hydrolysis of methyl formate is the main route for formic acid production.

The other processes for formic acid production include hydrolysis of formamide, but the formation of by-product ammonium sulfate made this process unattractive. Another process is oxidation of n-butane and naphtha where formic acid is obtained as by-product. But the advent of carbonylation of methanol to acetic acid process where formic acid is not obtained as a by-product resulted in the decrease of formic acid production through this route (Wells, 1999). Formic acid production through this route will continue to decline in future. A brief description of the production of formic acid by hydrolysis of methyl formate is described below. The process flow diagram for this process is shown in Figure 3.6.

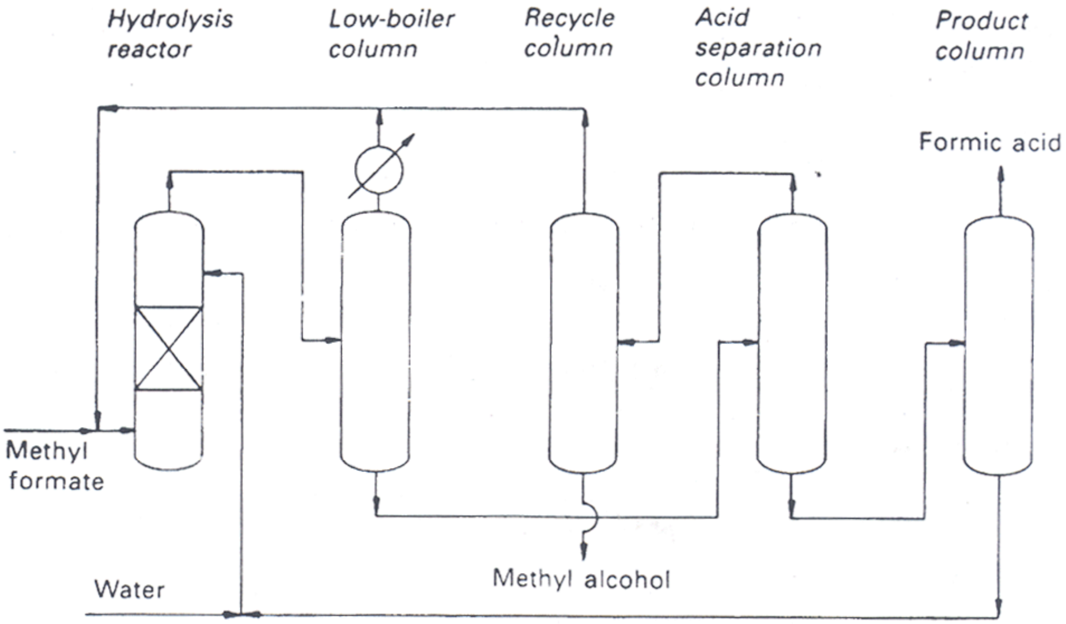


Figure 3.6. Formic Acid Production from Hydrolysis of Methyl Formate, from Wells, 1999.

In the hydrolysis of methyl formate process, methyl alcohol is reacted with dilute or impure anhydrous CO in the liquid phase at 80ºC and 45 bar pressure over sodium methoxide catalyst with 2.5% concentration. Methyl formate is the reaction product and unreacted CO is recycled. The conversion of the reaction is 64% per pass. Methyl formate is degassed and hydrolyzed with excess water to overcome the unfavorable equilibrium constant for methyl formate-formic acid reaction. The reaction is carried out at 80ºC and under increased pressure (Wells, 1999). The following reactions take place in the process.

$CH_3OH + CO \rightarrow HCOOCH_3$ $\Delta H^o = -46$ kJ/mol, $\Delta G^o = 2$ kJ/mol

$HCOOCH_3 + H_2O \rightarrow HCOOH + CH_3OH \quad \Delta H^o = 20$ kJ/mol, $\Delta G^o = 13$ kJ/mol

The reactor effluent contains unreacted water and methyl formate, and produced formic acid and methanol. The products are flashed off and separated by distillation column. Methyl alcohol and methyl formate are recovered overhead and recycled to the reactor. 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 (Wells, 1999). The equipment required for this process includes a hydrolysis reactor, low-boiler column, recycle column, acid separation column, and a product column (Wells, 1999).

Two potentially new processes that use carbon dioxide for the production of formic acid will be described, and compared to the above conventional process. The candidate processes will be selected for HYSYS simulation.

Thomas, et al., 2001 described a laboratory process for the synthesis of formic acid through CO_2 hydrogenation in liquid triethylamine. A trace amount of methanol was used as an additive, and $RuCl(O_2CMe)(PMe_3)_4$ was used as a catalyst. The composition of feed gas was represented in terms of partial pressures of the reacting components, which were 40 bar H_2 and 60 bar CO_2. The reaction was liquid phase and was operated at 50°C and 100 bar. 2.5 mmol methanol, 3.6 mmol liquid triethylamine, and 3.0 μmol catalyst were used in the reaction. The following reaction occurs in this study.

$CO_2 + H_2 + \frac{1}{2} N(C_2H_5)_3 \rightarrow \frac{1}{2} [HCOOH]_2N(C_2H_5)_3$

The rate was reported as the turnover frequency (TOF), meaning the number of turnovers per hour, where turnover number (TON) is mol of formic acid per mol of catalyst. The observed rate of the product is 3200 h^{-1} (Thomas, et al., 2001).

The above laboratory process is compared to the conventional process. The conventional process operates at 80°C whereas the laboratory process operates at 50°C. Thus, this experimental study operates at a lower temperature than the conventional process. The conventional process operates at a pressure of 45 bar whereas the laboratory process operates at 100 bar. Thus, the study operates at over twice the pressure of the conventional process.

The role of methanol was not clearly described as an additive and was speculated to interact with the catalyst in some manner. Yield was represented as the formic acid to triethylamine ratio. A highest ratio of 2:1 was possible but a more practically attainable ratio was 1.8:1. The author did not mention any separation techniques for the formic acid-triethylamine mixture. Conversion of the reactants in the reaction was also not mentioned. The catalyst used in the above study was active, very stable, and easy to prepare (Thomas, et al., 2001). In conclusion, this laboratory process is not selected for HYSYS simulation.

Dinjus, 1998, reviewed an experimental study for the production of formic acid through hydrogenation of carbon dioxide in aqueous solution. Water was used as a solvent in this research. Transition metal complexes are not suitable catalysts for use in aqueous solution for reasons of non-solubility. The catalyst that was found suitable and used was Wilkinson's catalyst [$ClRh(TPPTS)_3$]. The following reaction occurs in the reactor.

$CO_2\,(g) + H_2\,(g) \rightarrow HCOOH\,(l) \qquad \Delta H^o = -31$ kJ/mol, $\Delta G^o = 33$ kJ/mol

The author mentioned that high pressure and relatively low temperature are required to shift the equilibrium to the right. The reaction was operated at a temperature of 25°C and at a pressure of 40 bar. The rate of formation of formic acid was reported to be 3440 mol formic acid per mol of catalyst.

The above experimental study is compared to the conventional process. The conventional process operates at 50°C and 45 bar whereas the new potential process operates at 25°C and 40 bar. Thus, the new potential process operates at slightly lesser pressure and about half the temperature of the conventional process. The new potential process is advantageous from this point-of-view. Formic acid is formed at 3440 moles per mole of catalyst. The author did not mention the conversion of CO_2. The reaction is exothermic, and thus heat is liberated.

Industrial CO_2 removal from process waste streams is predominantly carried out in water (Dinjus, 1998). Thus, this experimental study, which takes place in aqueous solution, is an attractive starting point for the utilization of raw material CO_2 (Dinjus, 1998). In such a process, the purification costs for the raw material CO_2 can be eliminated. Consequently, this new potential process is selected for HYSYS simulation.

F) Acetic Acid

Acetic acid is present in the list developed by Pacific Northwest National Laboratory (PNNL) with a potential energy savings of 2 trillion BTUs per year through improved catalysts (Pellegrino, 2000). The three commercial synthetic routes for acetic acid production are oxidation of acetaldehyde, liquid-phase oxidation of n-butane or naphtha, and carbonylation of methyl alcohol. Because of its low material and energy costs and the absence of by-products, the Monsanto process for carbonylation of methyl alcohol is the dominant process (Wells, 1999). A brief description of this process is given below.

In the carbonylation of methyl alcohol, acetic acid is produced from methanol, carbon monoxide and water in a catalytic reactor operating at 450 K and 30 bar with essentially complete conversion of methanol in excess carbon monoxide (Moulijn et al., 2001). The process flow diagram for this process is shown in Figure 3.7. The following liquid-phase reaction takes place in the process.

$CO + CH_3OH \rightarrow CH_3COOH$ $\Delta H^o = -135$ kJ/mol, $\Delta G^o = -87$ kJ/mol

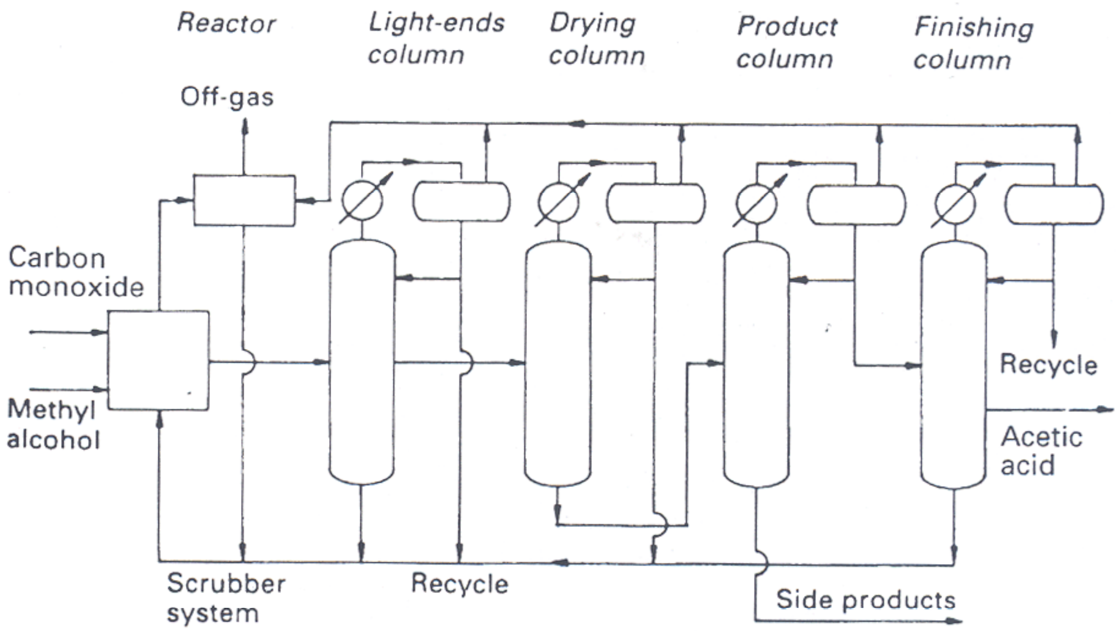


Figure 3.7. Monsanto's Process for Acetic Acid Production through Carbonylation of Methyl Alcohol, from Wells, 1999.

The hydrogen iodide catalyst is very active and corrosive, so resistant materials such as Hastelloy C and titanium are required. Water is required to suppress byproducts, and the separation of acetic acid and water is energy intensive requiring 5 kg steam per kg of dry acetic acid. The separation also requires large number of trays (Moulijn, et al., 2001). This equipment required for this process includes a reactor, a flash drum and four distillation columns.

Three potentially new processes, which use CO_2 as a feedstock, for the production of acetic acid will be described in brief. These two processes will be compared to the existing commercial process.

Taniguchi, et al., 1998, described acetic acid synthesis from methane and carbon dioxide in presence of vanadium catalysts. $VO(acac)_2$ (acac: acetylacetonate) was used as a catalyst. The reaction was carried out at 80°C (353K) and 25 atm (25 bar) pressure. The feed gas composition was 5 atm CH_4 (0.95 mmol) and 20 atm CO_2 (3.78 mmol). $K_2S_2O_8$ was added during the reaction as it acts as an oxidizing agent, and trifluoroaceticacid (TFA) was used as a solvent. A turnover number of 18.4 was observed and the reported acetic acid yield based on CH_4 was 97% (Taniguchi, et al., 1998). Acetic acid was produced according to the following reaction.

$$CH_4 + CO_2 \rightarrow CH_3COOH \qquad \Delta H^o = 36 \text{ kJ/mol}, \Delta G^o = 71 \text{ kJ/mol}$$

The experimental study is compared to the conventional process, and the following observations were made. The conventional process operates at 450 K and 30 bar whereas the study operates at 350 K and 25 bar. Thus, this potentially new process operates at a lower temperature and pressure than the conventional process. Conversion of methanol in the conventional process is 100% whereas conversion of methane is 97% in the case of this experimental study. Thus, conversions in both processes were comparable to each other. The study uses carbon dioxide and methane as raw materials, which are greenhouse gases whereas conventional process uses CO as a raw material, which is a toxic gas. Thus, this study uses carbon dioxide to replace toxic carbon monoxide. The reaction taking place in the conventional process is exothermic, but it is endothermic in case of this study. Therefore, energy has to be supplied to this reaction.

The catalyst used in the conventional process is corrosive, so resistant materials like titanium are required. In conclusion, this potentially new process is selected for HYSYS simulation.

Spivey, et al., described a laboratory process for acetic acid production from methane and carbon dioxide using 5% Pd/C catalyst. The reaction was carried out in a RGIBBS reactor in AspenPlus at 100-500°C and 10-150 atm. The feed gas composition was $CH_4/CO_2 = 95/5$. The author did not mention the conversion of methane or CO_2. The following reaction takes place in the process.

$CH_4 + CO_2 \rightarrow CH_3COOH$ $\Delta H^o = 36$ kJ/mol, $\Delta G^o = 71$ kJ/mol

The following observations were made based on the comparison between the new laboratory process and the conventional process. The operating temperature and pressure of the laboratory process are higher than that of both the conventional process and other new experimental studies described by Taniguchi et al., 1998. The inlet feed gas composition is $CH_4/CO_2 = 95/5$, which implies that large recycle volumes of excess CO_2 should be employed to increase the yield of product. In conclusion, this experimental study is not selected for HYSYS simulation.

Zerella, et al., 2003, described an experimental study for the production of acetic acid from methane and carbon dioxide using $K_2S_2O_8$, $VO(acac)_2$ as promoters. The reaction was carried out in a glass-lined autoclave at 80°C, and the feed gas composition was 80 psig CH_4 and 120 psig CO_2. $K_2S_2O_8$, $VO(acac)_2$ promoters were dissolved in an anhydrous acid (CF_3COOH, H_2SO_4, or CF_3SO_3H). The reported yield of acetic acid based on methane conversion was 40%. The following reaction occurred in the reactor.

$CH_4 + CO_2 + SO_3 \rightarrow CH_3CO_2SO_3H$
$CH_3CO_2SO_3H + H_2O \rightarrow CH_3COOH + H_2SO_4$

The above experimental study was compared with the conventional process and following observations were made. The conventional process operates at 450K and 30 bar, whereas the potentially new process operates at 353K (80°C) and 200 psig (20 bar). Thus, this process operates at lower temperature and pressure than the conventional process. The conversion of methanol in the conventional process is 100%. The yield of acetic acid based on methane conversion is 40%. Thus, the conversion in this potentially new process is low when compared to the conventional process. The study described by Taniguchi, et al., 1998, reported a conversion of methane to be 97%. This study described by Taniguchi, et al., 1998 was already selected for HYSYS simulation. Thus, this potentially new process was not selected for HYSYS simulation.

G) Styrene

Styrene is present in the list developed by Pacific Northwest National Laboratory (PNNL) with a potential energy savings of 20 trillion BTUs per year through improved catalysts (Pellegrino, 2000). The conventional processes for styrene include dehydrogenation of ethylbenzene. It is also obtained from ethylbenzene as a co-product of propylene oxide. About 87% of styrene worldwide is produced from dehydrogenation of ethylene, the remainder being obtained via the propylene oxide route (Wells, 1999). Styrene production from dehydrogenation of ethylbenzene will be briefly reviewed.

In the process for dehydrogenation of ethylbenzene, ethylbenzene is produced from catalytic alkylation of benzene with ethylene in liquid or vapor phase. The catalyst is either aluminum chloride promoted by HCl or ethyl chloride for the liquid-phase reaction, or crystalline aluminosilicate zeolite for the vapor phase process (Wells, 1999). The process flow diagram for this process is shown in Figure 3.8.

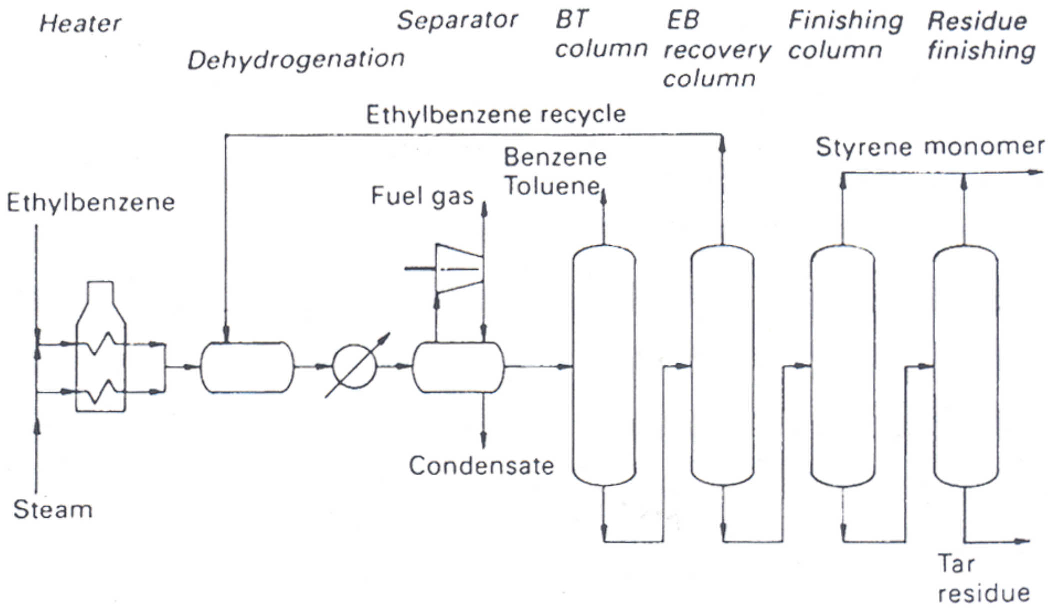


Figure 3.8. Styrene Production from Dehydrogenation of Ethylbenzene, from Wells, 1999.

The dehydrogenation reaction is carried out in an adiabatic fixed-bed reactor. Purified ethylbenzene is preheated with steam before entering a heat exchanger to increase the temperature further. The vapors are mixed with superheated steam, in the ratio of 2.6:1 steam:ethylbenzene by weight (Wells, 1999). The forward reaction is endothermic and requires large heat to be supplied. Low ethylbenzene partial pressures are preferred for equilibrium conversion of ethylbenzene. Superheated steam is thus used as a means of both supplying heat and lowering the partial pressure of ethylbenzene (Moulijn, 2001).

The gases are fed into a series of multiple beds containing dehydrogenation catalyst. Potassium carbonate promoted iron-chromium oxides or zinc oxide promoted with alumina or chromates is used as a catalyst. The reaction is operated at 690-700°C and below atmospheric pressure. Conversion levels of 50-70 wt% are observed with yields of 90-95 mol% (Wells, 1999). The following reaction occurs in the process.

$C_6H_5C_2H_5 \rightarrow C_6H_5C_2H_3 + H_2$ $\Delta H^o = 118$ kJ/mol, $\Delta G^o = 83$ kJ/mol

The effluent gases from the reactor are cooled and the heat recovered is used to generate steam or to preheat the reactor feed. Benzene and toluene are recovered by distillation under vacuum in the first column. Ethylbenzene and styrene are also separated by distillation under vacuum in the second column. In the third column styrene distillation is carried out in vacuum and as low a temperature as possible to reduce styrene polymerization. Typical production capacities of styrene range from 30,000 to 950,000 tonnes per year (Wells, 1999).

Several potentially new processes that use CO_2 for the production of styrene will be compared to the conventional process. Potential processes that have advantages over the conventional process will be selected for HYSYS simulation.

Sakurai, et al., 2000, described a method for the production of styrene through dehydrogenation of ethylbenzene using carbon dioxide. Vanadium oxide loaded with MgO (V/MgO-100A) was used as a catalyst. The reaction was carried out in a fixed bed flow type quartz reactor at 550°C and 1 atm pressure. The conversion of ethylbenzene, yield of styrene, and the selectivity of styrene observed were 59.1%, 53.8%, and 91.1% respectively (Sakurai, et al., 2000). During the reaction, carbon dioxide, corresponding to the amount of styrene produced, was reduced to carbon monoxide to give water (Sakurai et al., 2000). Styrene was produced according to the following reaction.

$C_6H_5C_2H_5 + CO_2 \rightarrow C_6H_5C_2H_3 + CO + H_2O$ $\Delta H^o= 159$ kJ/mol, $\Delta G^o = 112$ kJ/mol

The operating pressure of this study is in the same range as that of the conventional process (1 atm). The conventional process operates at a temperature of 690-700°C whereas the experimental study operates at 550°C. Thus, this reaction operates at a lower temperature than the conventional process even though more endothermic than that of conventional process based on their heats of reactions. The author did not mention the composition of feed gas. The conversion of ethylbenzene in both cases is in the same range. The yield of styrene in the study (53.8%) is less than that of the conventional process (90-95%), but this study uses carbon dioxide as a raw material. The major advantage of this research is that it operates at lower temperature and the major disadvantage is that the yield of styrene is low compared to the conventional process. CO and H_2O are obtained as by-products in this study whereas more valuable H_2 is obtained as by-product in the conventional process. In conclusion, this potentially new process is selected for HYSYS simulation.

Chang, et al., 1998, described an experimental study for the dehydrogenation of ethylbenzene with carbon dioxide over ZSM-5 zeolite-supported iron oxide catalyst. The reaction was carried out in a conventional flow-type reactor at 873 K (600°C) and 1 atm pressure. The main products of the reaction were styrene, carbon monoxide and water. The reported conversion of ethylbenzene and selectivity of styrene were 40% each. The composition of the feed gas was $CO_2/EB = 80$. The presence of carbon dioxide contributed to remarkable enhancement not only in dehydrogenation activity of catalyst but also of its coke resistance (Chang, et al., 2000). The following reaction occurs in the reactor.

$$C_6H_5C_2H_5 + CO_2 \rightarrow C_6H_5C_2H_3 + CO + H_2O \quad \Delta H^o = 159 \text{ kJ/mol}, \Delta G^o = 112 \text{ kJ/mol}$$

This study is compared to the conventional process. The operating temperature of in this reactor (600°C) is less than that of the conventional process (690-700°C) whereas both operate at 1 atm pressure. The ethylbenzene conversion (40%) is lower in the study than that of the conventional process (50-70%). The feed gas composition is CO_2/EB = 80, which implies that large volume of CO_2 will be present in the reactor effluent. Thus large recycle volumes of CO_2 are required for this potential process. Based on the heats of reactions, the reaction in this research is more endothermic than that of the conventional process. The styrene selectivity is 40% whereas the selectivity is 91% in the other study, which is already selected for HYSYS simulation. In conclusion, this experimental study is not selected for HYSYS simulation.

Mimura, et al., 1998, described a new method for the production of styrene through dehydrogenation of ethylbenzene using carbon dioxide. The Fe/Ca/Al oxides catalyst was found to exhibit high activity in the presence of CO_2. The reactor operates at 580°C and at 1 atm pressure. The feed gas composition was CO_2/EB = 9/1 and the observed yield of styrene was 70%, and the selectivity to styrene was 100%. The following reaction occurs in the reactor.

$$C_6H_5C_2H_5 + CO_2 \rightarrow C_6H_5C_2H_3 + CO + H_2O \quad \Delta H^o = 159 \text{ kJ/mol}, \Delta G^o = 112 \text{ kJ/mol}$$

The quantity of energy required in this research using CO_2 was much lower than that for the commercial process using steam, mainly because a large quantity of latent heat of water condensation cannot be recovered in the commercial process (Mimura, et al., 1998). The energies required for the commercial process using steam and for the potentially new process using CO_2 were estimated to be 1.5×10^9 cal/t-styrene and 6.3×10^8 cal/t-styrene respectively. Therefore, the potentially new process using CO_2 is an energy saving one compared to the existing commercial process (Mimura, et al., 1998).

The potentially new process operates at 580°C whereas the conventional process operates at 690-700°C. Thus, this reactor operates at a lower temperature than that of the conventional process. The yield of styrene observed in the experimental study is 70% at 580°C whereas it is 60% in the commercial process (Mimura, et al., 1998). This potentially new process may require less energy than the commercial process as discussed earlier. Consequently, this potentially new process is selected for HYSYS simulation.

H) Methylamines

The commercial process for the production of methylamines involves catalytic alkylation of anhydrous ammonia with methyl alcohol. All three amines (mono-, di-, and tri-methylamine) are formed in this process, and it is not economical to produce only one of the amines (Wells, 1999). However, di-methylamine is the most desired isomer. Another process for methylamines production uses formaldehyde and the reaction occurs in two stages. The choice of route varies from country to country, and depends mainly on cost of raw materials (Wells, 1999). The process that uses methyl alcohol will be described briefly here.

In this process, vaporized methyl alcohol and ammonia with a molar ratio 1:2 are preheated to 350°C under a pressure of 14 bar. The vapors are passed to a reactor, where reaction is carried out at 390-450°C and at a pressure of 14 bar. Amorphous silica-aluminum oxides, thorium oxide, chromium oxide, tungsten oxide, or a mixture of oxides can be used as catalyst. In most cases, amorphous silica-aluminum oxides will be used (Wells, 1999). The process flow diagram for this process is shown in Figure 3.9.

The reactor effluent containing methylamines, unreacted methyl alcohol, and ammonia are cooled and sent to a rectifier under 14 bar, where unreacted ammonia is removed and recycled back. The methylamine mixture from the bottom of the rectifier is extractively distilled under pressure with water, and tri-methylamine is recovered overhead (Wells, 1999). Mono-methylamine and di-methylamine are recovered by distillation in two separate columns. Most of the formed tri-methylamine is recycled back as the market demand is mainly for mono and di-methylamines. A total yield of 95% is obtained in this process. The following reactions occur in the process.

$CH_3OH + NH_3 \rightarrow CH_3NH_2 + H_2O$ $\Delta H^o = -17$ kJ/mol, $\Delta G^o = -17$ kJ/mol
$CH_3OH + CH_3NH_2 \rightarrow (CH_3)_2NH + H_2O$ $\Delta H^o = -37$ kJ/mol, $\Delta G^o = -30$ kJ/mol
$CH_3OH + (CH_3)_2NH \rightarrow (CH_3)_3N + H_2O$ $\Delta H^o = -46$ kJ/mol, $\Delta G^o = -36$ kJ/mol

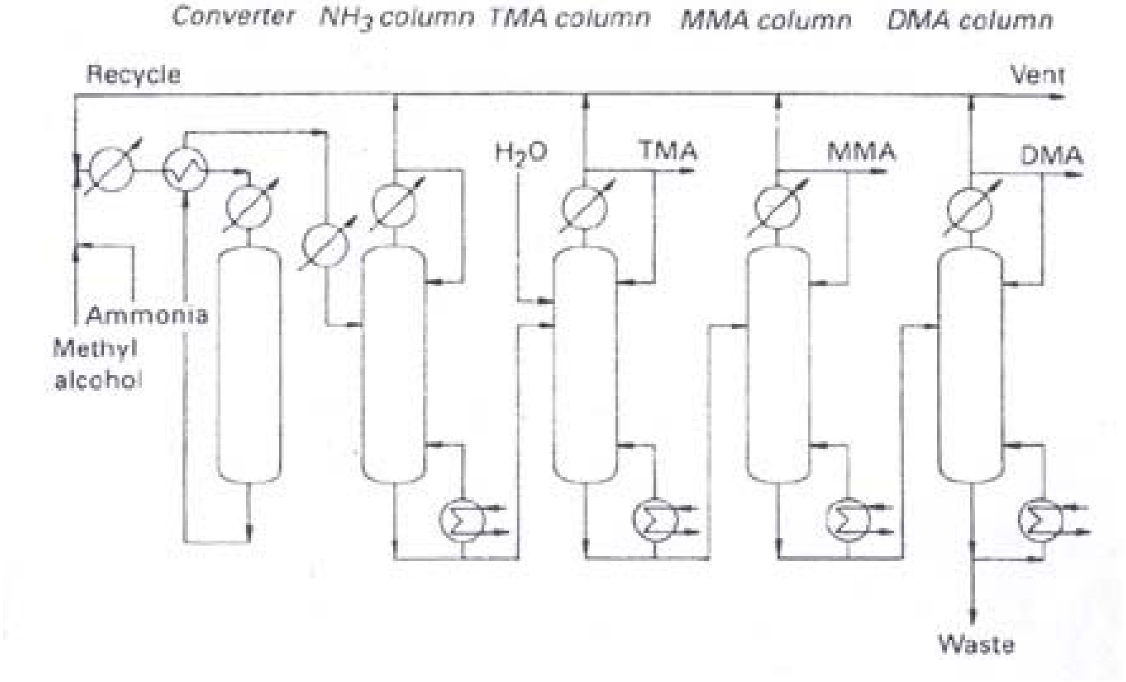


Figure 3.9. Methylamines Production from Catalytic Alkylation, from Wells, 1999.

A potentially new process that uses CO_2 for methylamines production are described. Arakawa, 1998, reviewed an experimental study for the production of methylamines from a mixture of CO_2, H_2, and NH_3. The catalyst used in this study was 51 wt% Cu/Al_2O_3, and the feed gas composition was $H_2/CO_2/NH_3 = 3/1/1$. Mono- and di-methylamines were produced effectively with by-product CO (Arakawa, 1998). The reaction was carried out at a temperature of 277°C and at a pressure of 0.6 MPa (6 atm or

6 bar). The author did not specify the conversion and product selectivity. The following reactions occur in this reactor.

$CO_2 + H_2 \rightarrow CO + H_2O$ ΔH^o= 41 kJ/mol, ΔG^o = 29 kJ/mol
$CO + 2H_2 \rightarrow CH_3OH$ ΔH^o= -90.5 kJ/mol, ΔG^o= -25 kJ/mol
$CH_3OH + NH_3 \rightarrow CH_3NH_2 + H_2O$ ΔH^o= -17 kJ/mol, ΔG^o = -17 kJ/mol
$CH_3OH + CH_3NH_2 \rightarrow (CH_3)_2NH + H_2O$ ΔH^o= -37 kJ/mol, ΔG^o= -30 kJ/mol

The above experimental study is compared to the conventional process. The conventional process operates at a temperature of 390-450°C and pressure of 14 bar whereas the potentially new process operates at 277°C and 6 bar. Thus, the new experimental study operates at a lesser temperature and pressure than the conventional process. The new study uses CO_2 as a raw material. In this research, methanol is produced in an intermediate step, which is the raw material in the conventional process. Based on the heats of reactions and Gibbs free energies, the reactions are thermodynamically feasible. In conclusion, this experimental study is selected for HYSYS simulation.

I) Lower Hydrocarbons

In this section, the processes for the production of lower hydrocarbons, mainly ethylene will be discussed. The other lower hydrocarbons such as methane, ethane, propane, and butane are constituents of natural gas. They can be obtained by separation of components of natural gas (Speight, 2002). Methane is the major component of natural gas.

In U.S. ethane is the prime feedstock for ethylene production, with 52% of ethylene produced by this route. However, in West Europe and Japan, naphtha is the prime feedstock (Wells, 1999). Ethylene plants based on ethane are cheaper to construct, easy to operate, and give high yields with minimal by-products (Wells, 1999).

Ethylene is produced from hydrocarbons (for example ethane or propylene) by steam cracking. In this process, hydrocarbon feedstock is mixed with steam to reduce the amount of coking in the tubular reactor, where the actual cracking takes place at a temperature of 750-870ºC (Wells, 1999). The reaction is endothermic, and requires considerable heat input. The amount of feedstock varies from 0.3 kg steam per kg ethane to 0.9 kg steam per kg gas oil (Speight, 2002).

The exit gases from the reactor are cooled to 550-600ºC, and compressed to 32-38 bar. The heat recovered is used to generate high-pressure steam. Hydrogen and methane are separated in a demethanizer. Bottoms from demethanizer are sent to deethanizer, where acetylene, ethylene, and ethane are separated overhead (Wells, 1999). The process flow diagram for this process is shown in Figure 3.10.

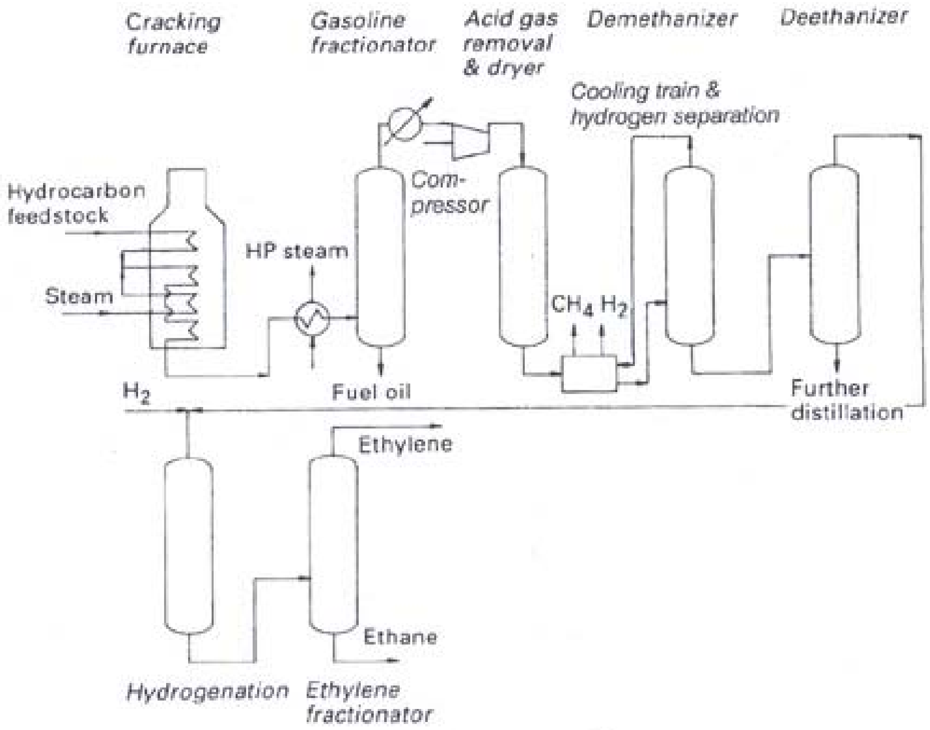


Figure 3.10. Ethylene Production by Steam Cracking of Hydrocarbons, from Wells, 1999.

Acetylene is hydrogenated and removed. Ethylene is recovered overhead and ethane in the bottom stream in a C_2 splitter by fractionation. The recovered ethane is recycled back to the reactor. Effluent from deethanizer is sent to depropanizer, where propane is separated from propylene, and recycled back to the reactor (Wells, 1999). The total yield of process is 30-35%. Propylene is produced according to the following reactions.

$C_2H_6 \rightarrow C_2H_4 + H_2$ $\Delta H^o = 136$ kJ/mol, $\Delta G^o = 100$ kJ/mol
$2C_3H_8 \rightarrow C_3H_6 + H_2 + C_2H_4 + CH_4$ $\Delta H^o = 205.5$ kJ/mol, $\Delta G^o = 127.5$ kJ/mol.

Nine potentially new processes that use carbon dioxide for the production of ethylene will be described. After comparing these with the above conventional process, candidate new processes will be selected for HYSYS simulation.

Wang and Ohtsuka, 2002, described a new laboratory process for co-production of ethylene and ethane from a mixture of CH_4 and CO_2. The feed gas composition was $CO_2/CH_4 = 2$. The reaction was carried out in a fixed-bed reactor at 800ºC and 1 atm over calcium based binary catalysts (CeO_2, Cr_2O_3, or MnO_2 with $Ca(NO_3)_2$). The author mentioned that the catalysts exhibited stable performances up to 10 hours. The yields of ethane and ethylene were reported to be 15% and 25% respectively (Wang and Ohtsuka, 2002). The following reactions occur in the reactor.

$2CH_4 + CO_2 \rightarrow C_2H_6 + CO + H_2O$ $\Delta H^o = 106$ kJ/mol, $\Delta G^o = 98$ kJ/mol
$2CH_4 + 2CO_2 \rightarrow C_2H_4 + 2CO + 2H_2O$ $\Delta H^o = 284$ kJ/mol, $\Delta G^o = 227$ kJ/mol

The potentially new process is compared to the existing commercial process. The conventional process operates at 750-870ºC, and this study operates at 800ºC. Thus, the operating temperatures of both are in the same range. The conventional process operates at a pressure of 32-38 bar (32-38 atm) whereas the experimental study operates at 1 atm.

Thus, this research operates at a much lower pressure than the conventional process. The yield of products is 30-35% in the conventional process, and the yields of ethane and ethylene were 15% and 25% respectively in the study. Thus, the yields were comparable to each other.

Based on the standard heats of reactions occurring in the study, the reactions are endothermic, and excess heat energy is to be supplied. The Gibbs free energies of reactions also suggest that these reactions are not thermodynamically promising. In conclusion, based on the above-mentioned reason, this study is not selected for HYSYS simulation.

Kim, et al., 1998, described another experimental study for the synthesis of lower olefins (C_2-C_4) by CO_2 hydrogenation over iron catalysts supported with potassium and supported with zeolite. A Fe-K/KY zeolite catalyst was used in this research. The reaction was carried out in a fixed-bed reactor at 573 K (300ºC) and 10 atm. The feed gas composition was $H_2/CO_2 = 3/1$, and $C_2 – C_5$ olefins were formed. The total hydrocarbon selectivity was 69.35%, and the selectivity for CO was 26.5%. The hydrocarbon distribution is given in Table 3.2. The total CO_2 conversion reported was 21.3% (Kim, et al., 1998).

Table 3.2. Distribution of Products among Total Hydrocarbons Produced (Kim, et al., 1998)

Methane	Ethylene	Ethane	Propene	Propane	Butene	Butane	C5>
11.2	9.1	2.1	13.6	2.3	10.8	2.75	47.6

The individual reactions for the formation of the products mentioned in Table 3.2 along with CO are presented below.

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ $\Delta H^o = -165$ kJ/mol, $\Delta G^o = -113$ kJ/mol
$2CO_2 + 6H_2 \rightarrow C_2H_4 + 4H_2O$ $\Delta H^o = -128$ kJ/mol, $\Delta G^o = -57$ kJ/mol
$2CO_2 + 7H_2 \rightarrow C_2H_6 + 4H_2O$ $\Delta H^o = -264$ kJ/mol, $\Delta G^o = -158$ kJ/mol

$3CO_2 + 9H_2 \rightarrow C_3H_6 + 6H_2O$ $\Delta H^o = -250$ kJ/mol, $\Delta G^o = -126$ kJ/mol
$3CO_2 + 10H_2 \rightarrow C_3H_8 + 6H_2O$ $\Delta H^o = -374$ kJ/mol, $\Delta G^o = -212$ kJ/mol
$4CO_2 + 12H_2 \rightarrow C_4H_8 + 8H_2O$ $\Delta H^o = -361$ kJ/mol, $\Delta G^o = -180$ kJ/mol
$4CO_2 + 13H_2 \rightarrow C_4H_{10} + 8H_2O$ $\Delta H^o = -486$ kJ/mol, $\Delta G^o = -269$ kJ/mol
$5CO_2 + 16H_2 \rightarrow C_5H_{12} + 10H_2O$ $\Delta H^o = -472$ kJ/mol, $\Delta G^o = -235$ kJ/mol
$CO_2 + H_2 \rightarrow CO + H_2O$ $\Delta H^o = 41$ kJ/mol, $\Delta G^o = 29$ kJ/mol

The above study is compared to the conventional process. The operating temperatures and pressures of conventional process are 750-870ºC and 32-38 atm whereas those of this study are 300ºC and 10 atm respectively. Thus, the new experimental study operates at lower temperature and pressure than that of conventional process. Along with ethylene, a variety of products (C_2-C_5 olefins) were formed in this study. The yield of products in the conventional process is 30-35%. The total conversion of CO_2 reported in this study was 21.3%, and the yield of C_2-C_4 olefins is 69.35%. Since a variety of products were formed in this study, therefore there were many reactions involved. Thus, even though the total CO_2 conversion was 21.3%, the specific conversions of CO_2 for each reaction would be low. For example, the specific conversion of CO_2 for the reaction for methane production was estimated to be only 1.65%.

Based on the heats of reactions and Gibbs free energies of the reactions of the study, the reactions are exothermic and thermodynamically feasible. The hydrogen to carbon dioxide ratio of 3:1 is typical in most CO_2 hydrogenation processes. In conclusion, because of low specific conversions of CO_2, this study is not selected for HYSYS simulation.

Xu, et al., 1998, described the results of an experimental study for the production of C_2-C_5 olefins through hydrogenation of carbon dioxide. The catalyst used was a Fe-Cu-Na/zeolite composite catalyst. The hydrogenation reaction was carried out at a temperature and pressure of 250ºC and 20 atm respectively. The feed gas composition was $H_2/CO_2 = 3/1$. The author reported a total CO_2 conversion of 12.5%. The selectivities of the products are 35.1% for C_1 olefins, 45.3% for C_2-C_5 olefins, and 14.8% for CO (Xu, et al., 1998). The following reactions occur, and other products were formed based on similar reactions.

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \Delta H^o = 41 \text{ kJ/mol}, \Delta G^o = 29 \text{ kJ/mol}$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \Delta H^o = -165 \text{ kJ/mol}, \Delta G^o = -113 \text{ kJ/mol}$$
$$2CO_2 + 6H_2 \rightarrow C_2H_4 + 4H_2O \qquad \Delta H^o = -128 \text{ kJ/mol}, \Delta G^o = -57 \text{ kJ/mol}$$
$$2CO_2 + 7H_2 \rightarrow C_2H_6 + 4H_2O \qquad \Delta H^o = -264 \text{ kJ/mol}, \Delta G^o = -158 \text{ kJ/mol}$$

The operating temperatures and pressures of conventional process are 750-870ºC and 32-38 atm whereas those of this study are 250ºC and 20 atm respectively. Though this research has advantages over the conventional process from temperature and pressure point-of-view, it is similar to the other study described by Kim, et al., 1998. The study described by Kim, et al., 1998 was also not selected for HYSYS simulation because of low specific conversions of CO_2. The study described by Kim, et al., 1998 has a CO_2 conversion of 21.3% whereas that described by Xu, et al., 1998 has a CO_2 conversion of only 12.5%. Consequently, this experimental study described by Xu, et al., 1998, is not selected for HYSYS simulation.

Nomura, et al., 1998, described a laboratory scale process for the synthesis of lower hydrocarbons by hydrogenation of carbon dioxide over a Fe promoted Cu-based catalyst. The hydrogenation reaction was carried out in a conventional flow reactor at a temperature and pressure of 553 K (280ºC) and 1 MPa (10 atm) respectively. The composition of the reactant gases was $H_2/CO_2 = 4/1$. The products of the reaction include CO, methanol, methane, ethane, propane, and butane with their selectivities being 60.5%, 5.2%, 17.3%, 6.6%, 5.8%, and 4.6% respectively. The reported conversion of CO_2 was 23.4% (Nomura, et al., 1998).

Though lower hydrocarbons were produced, the main product was CO with the highest selectivity among the products. The feed gas composition is $H_2/CO_2 = 4/1$, which suggests that this study requires more H_2 than typical CO_2 hydrogenation processes. Consequently, this study is not selected for HYSYS simulation.

Souma, et al., 1998, described the results of an experimental study for the production of hydrocarbons through hydrogenation of carbon dioxide. The CO_2 hydrogenation reaction was carried out in a fixed bed flow reactor for 6 hours at 350ºC and 50 atm. The reactant gas composition was $H_2/CO_2 = 3/1$. The reported CO_2 conversion was 40.9%. The specific conversion of CO_2 to CO was 26% and to that of hydrocarbons was 14.4%. The selectivities of methane, ethane, propane, and butane are 5%, 24%, 35%, and 24% respectively (Souma, et al., 1998).

This research operates at a higher pressure of 50 atm. The specific conversion of CO_2 to CO was more (26%) and to that of hydrocarbons (14.4%). Thus, CO is the major product rather than hydrocarbons. Moreover, the formed hydrocarbons are methane, ethane, propane, and butane. These are conventionally produced by separation of components of natural gas (Speight, 2002). In conclusion, this study is not selected for HYSYS simulation.

Habazaki, et al., 1998, described an experimental study for the production of methane by the hydrogenation of carbon dioxide. An amorphous Ni-Zr-rare earth element catalyst (Ni-30Zr-10Sm) was used in this study. The reaction was carried out in a fixed-bed flow reactor at an operating temperature of 473 K (200ºC). The author did not mention the operating pressure for the study. Two reactors in series with removal of water from the first reactor were used. The reported CO_2 conversion was 98%, and the feed gas composition was $H_2/CO_2 = 4/1$ (Habazaki, et al., 1998). The following reaction occurs in the reactor.

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ $\Delta H^o = -165$ kJ/mol, $\Delta G^o = -113$ kJ/mol

The above study uses a reactant gas of $H_2/CO_2 = 4/1$ as mentioned above, which suggests that the study uses more hydrogen than typical CO_2 hydrogenation processes. Also, the only product formed was methane. Methane is the main component of natural gas, and is conventionally produced by separating the components of natural gas. Therefore, it may not be economical to produce methane, using H_2 as a raw material. Moreover, this study uses more H_2 than typical CO_2 hydrogenation processes. Consequently, this study is not selected for HYSYS simulation.

Tan, et al., 1998, described a laboratory process for the production of iso-butane from CO_2 hydrogenation over a Fe-Zn-Zr/HY catalyst. The feed gas composition was $H_2/CO_2 = 3/1$. The hydrogenation reaction was carried out at a temperature of 360ºC and a pressure of 5 MPa (50 atm). The total conversion of CO_2 reported was 17.2%. The main products include CO, ethylene, propylene, and iso-butane. The selectivity to hydrocarbons was 46.8% and that to CO was 53.2%. The product distribution of hydrocarbons was methane (3%), iso-butane (38%), and ethylene and ethane (59%) (Tan, et al., 1998). The following reactions occur in the reactor.

$CO_2 + 3 H_2 \rightarrow CH_3OH + H_2O$ ΔH^o=-49 kJ/mol, ΔG^o=3kJ/mol (Fe-Zn-Zr catalyst)
$CO_2 + H_2 \rightarrow CO + H_2O$ $\Delta H^o = 41$ kJ/mol, $\Delta G^o = 29$ kJ/mol
$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$ $\Delta H^o = -24$ kJ/mol, $\Delta G^o = -17$ kJ/mol (HY catalyst)
$CH_3OCH_3 \rightarrow C_2H_4 + H_2O$ $\Delta H^o = -5$ kJ/mol, $\Delta G^o = -48$ kJ/mol
$C_2H_4 + CH_3OH \rightarrow C_3H_6 + H_2O$ $\Delta H^o = -5$ kJ/mol, $\Delta G^o = -48$ kJ/mol
$C_3H_6 + CH_3OH \rightarrow i\ C_4H_{1O}$

This experimental study is similar to the potentially new process described by Kim, et al., 1998, which was already selected for HYSYS simulation. This study operates at a temperature of 360ºC and 50 atm whereas the study described by Kim, et al., 1998 operates at 300ºC and 20 atm. The conversion of CO_2 in this study (17.2%) is less than the CO_2 conversion (21.3%) in the study described by Kim, et al., 1998. Also, C_5 hydrocarbons were formed in the study described by Kim, et al., 1998. But C_5 hydrocarbons were not formed in this study described by Tan, et al., 1998. Consequently, this experimental study is not selected for HYSYS simulation.

Zhang, et al., 2002, described the results of an experimental study for the production of ethane and propane from a two-step reaction sequence. Methane was used as a raw material, and a carbon supported Co catalyst was used in this study. In the first reaction, methane was decomposed to a reactive species CH_x and H_2. This reaction was carried out at a temperature range of 350-450ºC. Hydrogen was produced as an intermediate at a rate of 850 mmol/h-g-Co (Zhang, et al., 2002). However, the reactive species CH_x was not clearly defined. In the second reaction, CH_x was hydrogenated with the formed H_2 to produce ethane and propane. The second reaction was operated at a temperature of 100ºC. The author did not mention the operating pressures, and the conversions obtained in both the reactions. The author proposed the following reaction mechanism.

$$CH_4 \rightarrow CH_x + H_2$$
$$CH_x + H_2 \rightarrow C_2H_6 + C_3H_8$$

The above study does not use CO_2 as a raw material. Thus, this study cannot consume the excess high purity carbon dioxide available in the chemical complex in Lower Mississippi River Corridor. The operating pressures and conversions of the reactions were not mentioned. The reaction mechanism is also not clear. Consequently, this experimental study is not selected for HYSYS simulation.

Inui, 2002, reviewed the results of an experimental study for the synthesis of light olefins and gasoline from a mixture of CO_2 and H_2. The products are formed via methanol synthesis. The feed gas is a CO_2 rich synthesis gas with 22% CO_2, 3% CO, and 75% H_2O. Two reactors in series were used in this research. In the first reactor, methanol was produced as an intermediate from synthesis gas over Pd promoted Cu-Zn-Cr-Al-Ga mixed oxide catalyst. The operating temperature and pressure for this reaction were 543K (270ºC) and 7.8 MPa (78 atm) respectively. The conversion of reactants to methanol was 22% (Inui, 2002).

In the second reactor, H-Ga-Silicate catalyst was used. Light olefins (C_1-C_4) and gasoline were produced with a 100% methanol conversion. The second reaction was carried out at 573K (300ºC) and 1.5 MPa (15 atm). The reported gasoline selectivity was 53.6% (Inui, 2002).

The first reaction was operated at 78 atm pressure whereas the conventional process for methanol operates at 50-100 atm. Therefore, this study does not provide any advantage from this viewpoint. Also, the author mentioned that the reaction was operated at considerably low CO_2 conversion levels, and the selectivities of hydrocarbons were not high (Inui, 2002). In conclusion, the above experimental study is not selected for HYSYS simulation.

In summary, most of the experimental studies for the production of lower hydrocarbons (C_2 – C_5) have many reactions involved. Thus, even though the total conversion of CO_2 was high, but the specific conversions for individual reactions were low. Therefore, the experimental studies for lower hydrocarbons were not selected for HYSYS simulation.

J) Formaldehyde

Formaldehyde is present in the list developed by Pacific Northwest National Laboratory (PNNL) with a potential energy savings of 6 trillion BTUs per year through improved catalysts (Pellegrino, 2000). There are two commercial processes for the production of formaldehyde. Both these processes use methyl alcohol as a raw material. The first process involves partial oxidation – dehydrogenation with air in the presence of a silver catalyst, and is being practiced in major chemical companies like ICI, Degussa, and Borden. The second process, also called Formox process, involves complete oxidation with excess air in the presence of a metal oxide catalyst (Wells, 1999).

The metal oxide catalyst is less expensive than silver catalyst, and the complete oxidation process occurs at a lower temperature. Thus, the process using metal oxide catalyst has economic advantages over the partial oxidation-dehydrogenation route using a silver catalyst. However, the partial oxidation-dehydrogenation process is still the major process being practiced (Wells, 1999). This process will be described briefly, and the new processes that use CO_2 for the production of formaldehyde will follow this description.

In the partial oxidation-dehydrogenation process, excess pure methyl alcohol and air are fed into an evaporator. The vapor mixture is mixed with superheated steam and is sent into a reactor containing silver catalysts or layers of silver gauze. The oxidation reaction takes place at a temperature of 590-620ºC (Wells, 1999). The process operates at a pressure of 34-69 kPa (3.4-6.9 atm), and the methanol conversion per single pass is 65% (Speight, 2002). The process flow diagram for this process is shown in Figure 3.11. The following reactions occur in the process.

$$2CH_3OH + O_2 \rightarrow 2HCHO + 2H_2O \quad \Delta H^o = -299 \text{ kJ/mol}, \Delta G^o = -338 \text{ kJ/mol}$$
$$CH_3OH \rightarrow HCHO + H_2 \quad \Delta H^o = 92 \text{ kJ/mol}, \Delta G^o = 60 \text{ kJ/mol}$$

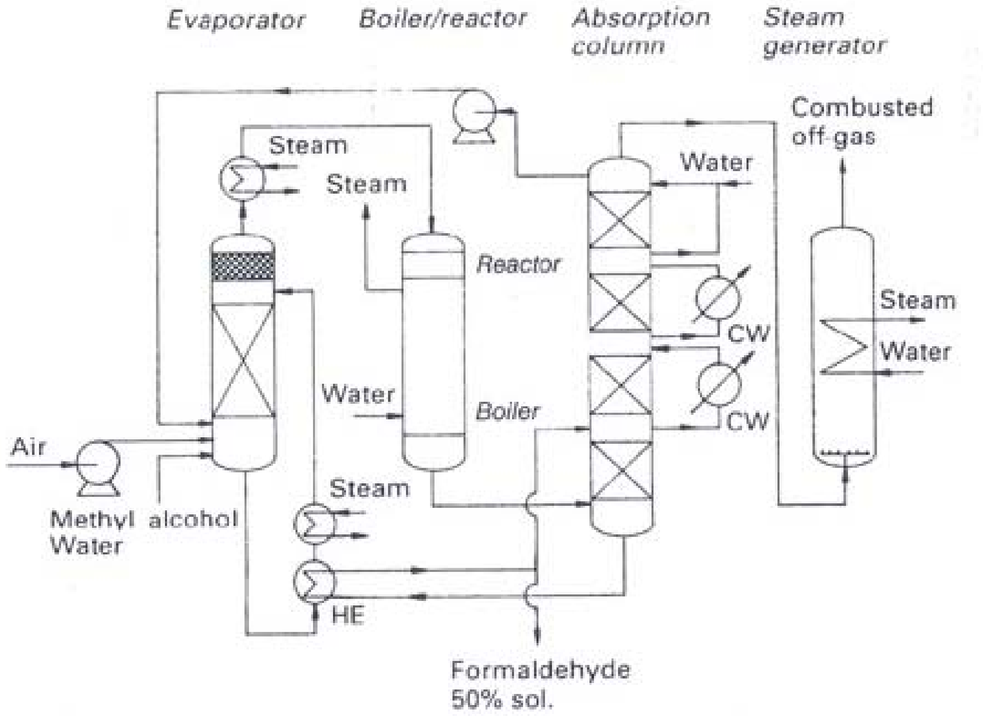


Figure 3.11. Formaldehyde Production by partial oxidation – dehydrogenation process, from Wells, 1999.

The reactor effluent containing formaldehyde, water, and unreacted methyl alcohol are cooled and condensed, and the heat recovered is used to generate steam. The effluent stream is sent to a distillation column, where unreacted methyl alcohol is recovered from the top and is recycled. Formaldehyde-water mixture obtained from the bottom is further distilled to increase the formaldehyde concentration (Wells, 1999). A yield of 89-92% is obtained typically, which largely depends on the feed concentration and the catalyst temperature (Wells, 1999). Formaldehyde is stable only in aqueous solution, commonly 37-56% formaldehyde by weight and often with methanol (3-15%) present as a stabilizer (Speight, 2002).

A potentially new process that uses CO_2 for the production of formaldehyde will be described now. The study will be compared to the existing commercial process.

Lee, et al., 2001, described a laboratory process for the selective production of formaldehyde from CO_2 hydrogenation. The hydrogenation reaction was carried out at a temperature of 423 K (150ºC) and at a pressure of 600 kPa (60 atm). The main product of the reaction was formaldehyde, although some methanol was formed. The catalyst used in this research was $PtCu/SiO_2$ with a ratio of Pt/Cu = 0.03 (Lee, et al., 2001). The following reaction takes place in the reactor.

$CO_2 + H_2 \rightarrow HCHO$ $\quad\quad \Delta H^o = 285$ kJ/mol, $\Delta G^o = 292$ kJ/mol

The conventional process operates at 590-620ºC and 3.4-6.9 atm whereas the laboratory process operates at 150ºC and 60 atm. Though the laboratory process operated at a lower temperature than the conventional process, it operated at a significantly higher pressure compared to the conventional process. In conclusion, this laboratory process is not selected for HYSYS simulation.

K) Graphite

Graphite is a soft, crystalline form of carbon that has different properties than amorphous carbon and diamond. Industrially, graphite is produced from retort or petroleum coke. This is a high temperature process and involves temperatures up to 2700ºC (Speight, 2002). The amorphous carbon is thus processed into graphite. Further process details were not available to mention.

$C(amorphous) \rightarrow C(graphite)$

Three new experimental studies that use CO_2 for the production of graphite will be described. Of these, the candidate processes will be selected for HYSYS simulation.

Nishiguchi, et al., 1998, described an experimental study for the synthesis of graphite carbon by reduction of carbon dioxide by catalytic fixation. Methane was formed as an intermediate. The study suggests a two-stage reaction mechanism with two reactors involved. In the first reactor, the recycled methane was decomposed into graphite carbon and hydrogen. Hydrogen produced was treated with CO_2 in the second reactor to produce methane and water. The formed methane was recycled back to the first reactor. The following reactions occur in this reactor.

$2CH_4 \rightarrow 2C + 4H_2$ $\Delta H^o = 150$ kJ/mol, $\Delta G^o = 101$ kJ/mol
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ $\Delta H^o = -165$ kJ/mol, $\Delta G^o = -113$ kJ/mol
Total: $CH_4\,(g) + CO_2\,(g) \rightarrow 2C\,(s) + 2H_2O\,(l)$ $\Delta H^o = -15.5$ kJ/mol, $\Delta G^o = -12$ kJ/mol

The study uses Ni supported SiO_2 catalyst for both the reactions. The author mentioned that the activity of catalyst was stably sustained over long period. The study operates at 500ºC and at atmospheric pressure, and the observed conversion of CO_2 to graphite carbon was 70%. The feed gas composition was $H_2/CO_2/N_2 = 4/1/3$ (Nishiguchi, et al., 1998).

The conventional process operates at 2700ºC whereas the new study operates at 500ºC. Thus, this potentially new process is more advantageous from this viewpoint. The study operates at atmospheric pressure, thus it is not operating at high pressures. The CO_2 conversion reported was 70% and the catalyst activity was mentioned to be stable for a long period. The heats of reactions and Gibbs free energies suggest that both the reactions are thermodynamically feasible. In conclusion, this new experimental study is selected for HYSYS simulation.

Arakawa, 1998, reviewed the results of an experimental study for the conversion of carbon dioxide to graphite carbon via CO by direct hydrogenation. Carbon dioxide was converted to graphitic carbon with 40% selectivity, and the observed conversion of carbon dioxide was 60%. A WO_3 or Y_2O_3 catalyst was used, and the hydrogenation reaction operates at 700ºC and 0.1 MPa (1 atm). The feed gas composition was $H_2/CO_2/N_2 = 2/1/5$.

This study operating at 700°C operates at a lower temperature than the conventional process, which operates at 2700°C. But the previous study described by Nishiguchi, et al., 1998 operates at a much lower temperature of 500°C, and was already selected for HYSYS simulation. The conversion of CO_2 to graphite in the study described by Nishiguchi, et al., 1998 was 70%, but it was 60% in the study reviewed by Arakawa, 1998. Thus, the study reviewed by Arakawa, 1998, operates at a higher temperature and lower conversion than the study described by Nishiguchi, et al., 1998. But the study described by Nishiguchi, et al., 1998, requires more H_2 than that reviewed by Arakawa, 1998. However, since H_2 is obtained as an intermediate, this does not affect the economics of the process.

In conclusion, the study reviewed by Arakawa, 1998, did not have the advantages that the study described by Nishiguchi, et al., 1998, has. Consequently, this new study was not selected for HYSYS simulation.

Motiei, et al., 2001, described a laboratory process for synthesizing carbon nanotubes and nested fullerenes from supercritical CO_2 by a chemical reaction. The study operates at 1000°C and 10 kbar, and the yield of nanotubes observed was 15%. The author mentioned that it was not clear whether the reaction was catalyzed by any of the components of the stainless steel cell, in which the reaction was carried out. Also the author mentioned that 59% of the gases leaked out during the reaction because of the high pressure involved. The following reactions occur in this study.

$$\text{Mg (g)} + \text{CO}_2\text{ (g)} \rightarrow \text{MgO (g)} + \text{CO (g)}$$
$$\text{Mg (l)} + \text{CO (g)} \rightarrow \text{MgO (g)} + \text{C (graphite)}$$

Though, this study operates at a lower temperature than the conventional process (2700°C), it operates at much higher temperature than the study described by Nishiguchi, et al., 1998, operating at 500°C. The study described by Nishiguchi, et al., 1998 was already selected for HYSYS simulation. The catalytic effect of the stainless steel cell on the reaction was also not clear. In conclusion, this new laboratory process is not selected for HYSYS simulation.

L) Hydrogen

The conventional process for the production of hydrogen will be described briefly. Hydrogen is conventionally produced by steam reforming of natural gas (CH_4) following a two-step reaction sequence involving reforming and shift conversion. The following reactions occur in the process.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H^o = 206 \text{ kJ/mol}, \Delta G^o = 142 \text{ kJ/mol}$$
$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H^o = -41 \text{ kJ/mol}, \Delta G^o = -29 \text{ kJ/mol}$$

In this process, natural gas is first desulphurized by heating to 370ºC in the presence of a metal oxide catalyst. The natural gas feedstock is mixed with steam in a furnace, and the reforming reaction takes place at 760-980ºC and 600 psi (41 atm) over a nickel catalyst. Synthesis gas containing a mixture of CO and H_2 is formed (Speight, 2002). The reactor effluent enters a shift converter where it is mixed with more steam. Carbon monoxide reacts with steam to produce hydrogen and CO_2 over iron or chromic oxide catalysts at 425ºC (Speight, 2002).

The conventional catalyst has no ability for CO_2 activation. CO_2 once formed by shift reaction cannot be converted to other molecules by the reaction between CO_2 formed and unreacted methane (Inui, 2002). To separate CO_2 and H_2, the products are cooled to 38ºC and sent to an absorber where monoethanolamine is used to absorb CO_2.

The by-product CO_2 is later separated by desorption by heating the monoethanolamine (Speight, 2002). Thus, the conventional process produces CO_2 as a by-product.

Fourteen potentially new processes that use CO_2 for the production of either pure H_2 or synthesis gas through reforming of methane will be described in brief. These new laboratory processes produce synthesis gas, which is a mixture of CO and H_2, but do not produce pure H_2. However, the produced synthesis gas is a good source of H_2 for the chemical complex. These potentially new processes will be compared to the existing commercial process. Experimental studies having advantages over the commercial process will be selected for HYSYS simulation.

Song, et al., 2002, described two experimental studies for the production of CO rich synthesis gas from CO_2 reforming of methane. In the first study, a feed gas containing equimolar methane and CO_2 were mixed at 750ºC and 1 atm. The catalyst used in this study was 8 wt% Ni/Na-Y. The reported conversions of CO_2 and methane were 91.1% and 89.1% respectively. The observed yields of products CO and H_2 were 85.6% and 69% respectively. The distribution of the gases in the produced synthesis gas was $H_2/CO = 0.80$ (Song, et al., 2002).

In the second study, a feed gas containing equimolar methane and CO_2 were mixed at 750ºC and 1 atm. The catalyst used in this study was 6.6 wt% Ni/Al_2O_3. The reported conversions of CO_2 and methane were 91.8% and 95.3% respectively. The observed yields of products CO and H_2 were 82% and 66% respectively. The distribution of the gases in the produced synthesis gas was $H_2/CO = 0.81$ (Song, et al., 2002). The following reaction was involved in both the studies.

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \qquad \Delta H^o = 247 \text{ kJ/mol}, \Delta G^o = 171 \text{ kJ/mol}$$

Both the studies operate at the same temperature and pressure of 750ºC and 1 atm. However, the conversions of both CO_2 and methane are slightly higher in the study where Ni/Al_2O_3 catalyst was used. The conventional process for the production of H_2 operates at 760-980ºC and 41 atm whereas the study operates at 750ºC and 1 atm. The conventional process produces CO_2 as a by-product whereas the new study uses CO_2 as a raw material. In conclusion, the study that use Ni/Na-Y catalyst is not selected for HYSYS simulation, and the study that uses Ni/Al_2O_3 catalyst is selected for HYSYS simulation.

Inui, 2002, described a laboratory scale process for the production of synthesis gas through CO_2 reforming of methane. In the first study, the reaction was carried out over Rh-modified Ni-Ce_2O_3-Pt catalyst (10 wt% Ni – 6 wt% Ce_2O_3) at 873 K (600ºC). The composition of the feed gas was $CH_4:CO_2:N_2$ = 10:10:80. The reported conversion of methane was 65%. The following reaction was involved in the study.

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \qquad \Delta H^o = 247 \text{ kJ/mol}, \Delta G^o = 171 \text{ kJ/mol}$$

The author did not mention the role of N_2 in the reaction. The operating pressure was also not mentioned. The study operates at 600ºC, and the conventional process operates at 760-980ºC. However, the conversion of methane was 65%, and it was 95% in the earlier process by Song, et al., 2002. Hence, this study is not advantageous than the process described by Song, et al., 2002. Consequently, it is not selected for HYSYS simulation.

Inui, 2002, described another two experimental studies for the production of synthesis gas. In the first study, the author studied the effect of catalytic oxidation of propane on the CO_2 reforming of methane over a Rh-modified four-component catalyst. The feed gas composition was 35% CH_4, 10% CO_2, 3.3% C_3H_8, 16.5% O_2, and 35.2%

N_2. The reactor was operated at 700ºC and 1 atm. The observed conversion of methane was 80.8%.

In the second study, effect of ethane addition to the CO_2 reforming of methane over the same catalyst was studied. The feed gas composition was 35%CH_4, 10% CO_2, 5% C_2H_6, 17.5% O_2, and 32.5% N_2. The reactor was operated at 700ºC and 1 atm. The observed conversion of methane was 82.2% (Inui, 2002).

Both the studies operate at 700ºC and 1 atm, whereas the conventional process operates at 760 - 980ºC and 41 atm. The author did not mention the reaction mechanism occurring in both the studies. The studies use more methane than CO_2 in the feed. Also, the roles of O_2 and N_2 were not clear. These two experimental studies are not selected for HYSYS simulation.

Shamsi, 2002, performed three experimental studies on CO_2 reforming of methane to produce synthesis gas with three different catalysts. The following reaction was involved in all three studies.

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \qquad \Delta H^o = 247 \text{ kJ/mol}, \Delta G^o = 171 \text{ kJ/mol}$$

In the first study, the reaction was carried out in a fixed bed reactor at 850ºC and 1 atm over tungsten carbide catalyst. The reported conversions of methane and carbon dioxide were 90.7% and 99.7% respectively. The yield of product CO was 87%, and the product ratio of hydrogen and CO was 1.1. The composition of the feed gas was $CO_2/CH_4 = 1.15$.

The above study operates in the same temperature range as the conventional process, but it operates at a much lower pressure (1 atm) than the conventional process (41 atm). However, the author mentioned that catalyst was irreversibly deactivated after

35 hours on stream, and regeneration was not possible. Hence, this study is not selected for HYSYS simulation.

In the second study, the reaction was operated in a fixed bed reactor at 750ºC and 1 atm over a commercial nickel-based catalyst (R-67). The reported conversions of methane and carbon dioxide were 94% and 91% respectively. Equimolar product ratio was obtained, and the yield of CO was 95%. The composition of the feed gas was $CO_2/CH_4 = 1.15$.

Though this study has an advantage of operating at low pressure, the author reported that the catalyst produced significant amount of carbon in the catalyst bed. This eventually plugged the reactor and stopped the flow (Shamsi, 2002). Hence, this study is not selected for HYSYS simulation.

In the third study, the reaction was operated in a fixed bed at 850ºC and 1 atm over a noble metal catalyst of 1% rhodium supported on alumina. The observed conversions of methane and CO_2 were 97% each. The reported yield of CO was 96%, and equimolar product ratio was obtained.

The new experimental study operates in the same temperature range as the conventional process. It operates at 1 atm whereas the conventional process operates at 41 atm. As mentioned above, the conversions of both methane and CO_2, and the product yields are high. The rhodium catalyst is more expensive than nickel-based and carbide catalysts used in the previous studies (Shamsi, 2002). However, it is more stable and produces no carbon during the reaction. The high cost of rhodium metal could be tolerated considering higher activity, low metal loading, and reduced carbon deposition (Shamsi, 2002). Consequently, the new study is selected for HYSYS simulation.

Wei, et al., 2002 s, described an experimental study for the production of synthesis gas through reforming of methane over Ni supported ultra fine ZrO_2 catalyst. The catalyst exhibited a life longer than 600h without any deactivation. The reactor was operated at 1030K (757°C) and atmospheric pressure. The feed gas is an equimolar mixture of methane and carbon dioxide. The reported conversions of methane and CO_2 were 86.2% and 88.3% respectively. The reported selectivities to CO and H_2 were 95.4% and 79.5% respectively. The distribution of CO and H_2 in the produced synthesis gas was $CO/H_2 = 1.2$, which is more desirable for oxo synthesis, oxygenates, and long chain hydrocarbons (Wei, et al., 2002). The following reaction occurs in the reactor.

$CH_4 + CO_2 \rightarrow 2H_2 + 2CO$ $\quad\quad \Delta H^o = 247$ kJ/mol, $\Delta G^o = 171$ kJ/mol

The new study operates at 757°C and 1atm whereas the conventional process operates at 760-980°C and 41 atm. Thus, the study operates at a much lower pressure than the conventional process. The author reported that the catalyst exhibited a long life of over 600h without any deactivation. The conversion of methane was 86.2%, which is reasonably high. Consequently, this potentially new process is selected for HYSYS simulation.

Nakagawa, et al., 2002, described two laboratory scale processes for synthesis gas production. In the first study, reforming of methane was carried over Ru loaded La_2O_3 catalysts. The reaction was carried out in a fixed bed flow type quartz reactor at 600°C and 1 atm. The feed contains an equimolar mixture of methane and carbon dioxide. The conversions of methane and CO_2 were 28% and 33% respectively. The yields of H_2 and CO were 25.4% and 30.5% respectively. The distribution of H_2 and CO in the synthesis gas was $H_2/CO = 0.83$. The following reaction occurs in both the studies.

$CH_4 + CO_2 \rightarrow 2H_2 + 2CO$ $\Delta H^o = 247$ kJ/mol, $\Delta G^o = 171$ kJ/mol

In the second study, the reaction was carried out in the same conditions as in the previous study. The catalyst used in this study was a Ru loaded Y_2O_3 catalyst. The conversions of methane and CO_2 were 30% and 35.5% respectively. The yields of H_2 and CO were 27% and 32.7% respectively. The distribution of H_2 and CO in the synthesis gas was $H_2/CO = 0.83$ (Nakagawa, et al., 2002).

Both the studies operate at 600°C and 1 atm, whereas the conventional process operates at 760-980°C and 41 atm. Thus, these studies have the advantage of operating at lower temperature and pressure compared to the conventional process. But, as mentioned above, the conversions of CO_2 and methane in both the processes were lower than the other new studies selected for HYSYS simulations. Thus, both these experimental studies are not selected for HYSYS simulations.

Effendi, et al., 2002, described an experimental study for the production of synthesis gas through reforming of methane over $Ni/SiO_2 - MgO$ catalyst. A fluidized bed reactor was used in this study. The reactor was operated at 700°C and 1 atm, and the feed gas composition was $CO_2/CH_4 = 0.84$. The conversions reported for methane and CO_2 were 37.7% and 52.7% respectively. The distribution of products in the synthesis gas was $H_2/CO = 0.69$. The following reaction occurs in the reactor.

$CH_4 + CO_2 \rightarrow 2H_2 + 2CO$ $\Delta H^o = 247$ kJ/mol, $\Delta G^o = 171$ kJ/mol

The new study operates at a lower pressure (1 atm) compared to the conventional process (41 atm). But the conversions of CO_2 and methane were lower when compared to the other new studies that were already selected for HYSYS simulations. The feed composition mentioned above suggests that this study uses more methane than CO_2. The product distribution also suggests that the H_2 produced is less when compared to the other new studies. Consequently, this study is not selected for HYSYS simulation.

Tomishige, et al., 1998, described a laboratory scale process for the production of synthesis gas by reforming of methane over a nickel-magnesia solid solution catalyst. The reaction was operated at 1123 K (850°C) and 0.1 MPa (1 atm) in a fixed bed flow reactor. The feed gas is an equimolar mixture of CH_4 and CO_2. The reported conversion of methane was 80%. The author also mentioned that the catalyst used in this study was inexpensive compared to the other commercial catalysts, and was effective in preventing the coke deposition inside the reactor. The following reaction occurs in the reactor.

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \qquad \Delta H^o = 247 \text{ kJ/mol}, \Delta G^o = 171 \text{ kJ/mol}$$

This study operates at 850°C and 1 atm, whereas the conventional process operates at 760 - 980°C and 41 atm. Thus, the study operates at a lower pressure than the conventional process. The conversion of methane (80%) was reasonably high. Also, the catalyst demonstrated effectively in preventing the coke deposition inside the reactor. Thus, this potentially new process is selected for HYSYS simulation.

M) Other Reactions

The other reactions that were listed in Chapter Two include Electrochemical reactions, photocatalytic reactions, polymerization reactions, and supercritical CO_2 reactions. The numerous published articles in this category that use CO_2 as a feedstock were briefly mentioned in Chapter Two. Presently, simulating these experimental studies using HYSYS is not possible to estimate the energy requirements and perform the value-added economic analysis. Thus, these studies will not be incorporated in the superstructure at this point in time.

N) Summary

Potentially new processes that use carbon dioxide as a feedstock were selected to incorporate in the superstructure. These laboratory scale processes were simulated to industrial scale using HYSYS. A methodology for selecting the new energy efficient processes was developed. The selection criteria for a new experimental study to be simulated using HYSYS includes operating conditions like temperature and pressure, catalyst performance, cost of raw materials, and demand of products. The thermodynamic feasibility of reactions involved and the by-products obtained were also considered for selecting potentially new processes. These new experimental studies were compared to the existing commercial processes. New experimental studies demonstrating advantages over the conventional processes were selected for HYSYS simulation. Also, a potentially new process for propylene production through propane dehydrogenation was selected because it provides a source for hydrogen in the super structure.

Pacific Northwest National Laboratory (PNNL) estimated potential energy savings for 26 commercial chemicals through improved catalysts (Pellegrino, 2000). Propylene, methanol, acetic acid, styrene, and formaldehyde were on this list with a potential energy savings of 98, 37, 2, 20, and 6 trillion BTUs per year respectively.

Twenty potentially new processes were selected for HYSYS simulation to be integrated in the chemical complex based on the selection criteria discussed earlier. These potentially new processes are listed in Table 3.3. The selected processes include five new experimental studies for methanol production, and four new studies for synthesis gas production. Also, they include new studies for propylene, ethanol, styrene, formic acid, acetic acid, dimethyl ether, graphite and methylamines production.

Table 3.3. Potentially New Processes Selected for HYSYS Simulation.

Chemical	**Synthesis Route**	**Reference**
Methanol	CO_2 hydrogenation	Nerlov and Chorkendorff, 1999
	CO_2 hydrogenation	Toyir, et al., 1998
	CO_2 hydrogenation	Ushikoshi, et al., 1998
	CO_2 hydrogenation	Jun, et al., 1998
	CO_2 hydrogenation	Bonivardi, et al., 1998
Ethanol	CO_2 hydrogenation	Inui, 2002
	CO_2 hydrogenation	Higuchi, et al., 1998
Dimethyl Ether	CO_2 hydrogenation	Jun, et al., 2002
Formic Acid	CO_2 hydrogenation	Dinjus, 1998
Acetic Acid	From methane and CO_2	Taniguchi, et al., 1998
Styrene	Ethylbenzene dehydrogenation	Sakurai, et al., 2000
	Ethylbenzene dehydrogenation	Mimura, et al., 1998
Methylamines	From CO_2, H_2, and NH_3	Arakawa, 1998
Graphite	Reduction of CO_2	Nishiguchi, et al., 1998
Hydrogen/Synthesis Gas	Methane reforming	Song, et al., 2002
	Methane reforming	Shamsi, 2002
	Methane reforming	Wei, et al., 2002
	Methane reforming	Tomishige, et al., 1998
Propylene	Propane dehydrogenation	Takahara, et al., 1998
	Propane dehydrogenation	C & EN, June 2003, p. 15

The evaluations of the HYSYS simulations will be discussed in the next chapter. The energy requirements will be estimated, and a value-added economic analysis will be evaluated for all these potentially new processes. These new studies will be incorporated in the super structure, and the results will be discussed in Chapter Four.

CHAPTER FOUR: RESULTS FROM EVALUATING NEW PROCESSES

The methodology for the selection of potentially new processes was discussed in Chapter Three. Twenty potentially new processes were selected, and these include processes for methanol, ethanol, dimethyl ether, formic acid, acetic acid, styrene, methylamines, graphite, hydrogen, and propylene. The selected new experimental studies were simulated using HYSYS, and their results are discussed in this chapter. Based on these results, promising potentially new processes are selected and integrated into the chemical production complex in lower Mississippi River Corridor.

A) Economic Analysis

A value-added economic analysis was used for each HYSYS simulation, and this analysis required specifying product price and sales, raw material cost and use, and utility costs. The other operating costs that go into the total product cost, and a return on investment for the plant cost were not included. These costs reduce the profit expected based on the value added economic model. If a process is not profitable based on the value added economics, it will not be profitable with the other costs included. A general procedure for evaluating value added economic cost analysis is given by the equation:

$$\text{Profit} = \Sigma \text{ Product Sales} - \Sigma \text{ Raw Material Costs} - \Sigma \text{ Energy Costs} \qquad (4.1)$$

Details for the evaluation are given in Appendix C, and the new acetic acid process is used to illustrate the evaluations. All of the sales prices and costs are tabulated in this appendix.

Product sales prices and raw material costs used in this research were obtained from the Chemical Market Reporter (Chemical Market Reporter, February, 2002), Turton, et al., 1998, and Camford Chemical Prices, 2000. Plant production capacities were based on plants in the lower Mississippi River Corridor or an average production capacity in the U.S.

The raw material cost for CO_2 was \$3.00 per ton, the cost of delivering it from a pipeline (Hertwig, T. A., Private Communication, 2003). The CO_2 feed used in all the processes was at 100 psi and 30 ºC, pipeline pressure and temperature.

The cost of CO (\$31 per ton) was not available from the Chemical Market Reporter, and it was based on its heating value as a fuel as shown in Appendix A. The cost of pipeline hydrogen (\$796 per ton) is based on the cost of methane as given by Kuehler, G. P., Private Communication**,** 2003. The estimation of cost for hydrogen is shown in Appendix B.

For steam, it was used in the form of high-pressure (HP) steam for process heating. The conditions for HP steam are 47 bar, 260ºC, and with a specific heat of 1.067 kcal/kg ºC. The heat of vaporization of HP steam was used to supply the required process energy. The heat of vaporization of HP steam is 1661.5 kJ/kg (Smith, et al., 1996). The cost of HP steam is \$8.65 per ton (Turton, et al., 1998). Natural gas, or fuel oil are required to produce steam, and cooling towers are used to cool water.

Cooling water was used in heat exchangers and condensers where energy was removed from process streams, and it was heated from 30ºC to 50ºC. Excess scaling occurs above this temperature (Turton, et al., 1998). The cost of cooling water is \$ 6.7 per 1000m^3 (Turton, et al., 1998).

B) HYSYS Simulations

HYSYS is a flow sheeting program that can be used to create rigorous steady-state and dynamic models for plant design. HYSYS has been developed by Hyprotech, a leading supplier of modeling and simulation software. The HYSYS version used in this research for simulating the potentially new processes was HYSYS.Plant.2.2. HYSYS.Plant.2.2 provides an integrated steady-state and dynamic simulation capability, offers rigorous and high-fidelity results with a fine level of equipment geometry and performance detail (HYSYS Documentation Users Manual).

For all of the HYSYS simulations in this chapter, conversion reactor was used to simulate the reactors. Most of the experimental studies listed in Chapter Two and Three, the conversion of the reactants was given. Other reactor options are equilibrium and kinetic reactors. For estimating the steam and cooling water requirements, heat exchangers were used.

In the HYSYS simulations given in this research, plants producing the same product did not have the same production capacity. This is because the product flow rate depends on the purity of the product. A slight change in the purity of the product changes its production flow rate, and hence the production capacity. For most of the HYSYS simulations, distillation columns were used for separation of products from reactors. However, for all of the HYSYS simulations the purity of the product in all plants was close to each other. For example, the purity of methanol in all of the five HYSYS simulations ranged from 98.9 to 99.1%. Thus, these plants were simulated in such a way that the production capacities of plants producing the same product were close to each other to the extent possible.

All of the HYSYS simulations given in this chapter are included on the CD with this thesis. The results of the studies of the simulated processes that use carbon dioxide are given now, and the results for propylene production are described first. The reaction mechanisms, catalyst used, and the conversions obtained for each process are given in this chapter. A more detailed description of these experimental studies was given in Chapter Three.

C) Propylene Production

Two potentially new processes for propylene production were simulated using HYSYS. The results of these simulations are described below.

1) Propylene from Propane and CO_2

The experimental study described by Takahara, et al., 1998, for the production of propylene using CO_2 over a Cr_2O_3/SiO_2 catalyst was simulated using HYSYS. The chemical reaction occurred is:

$$C_3H_8 + CO_2 \rightarrow C_3H_6 + CO + H_2O \quad \Delta H^o = 165 \text{ kJ/mol}, \Delta G^o = 114.8 \text{ kJ/mol}$$

The plant capacity used in this simulation was 41,900 metric tons of propylene per year (4,784 kg/hr). This was based on Union Texas Ethylene Corporation plant, located in Geismar, LA, that produces propylene at a production capacity of 92 million lb/year (41,732 metric tons/year) (Louisiana Chemical & Petroleum Products List, 1998).

The HYSYS flow diagram for this potentially new process is shown in Figure 4.1. The conversion of propane was 45% (Takahara, et al., 1998). The unreacted propane and CO_2 were recycled, and 100% conversion was obtained, as shown in Figure 4.1.

Using HYSYS flow sheet, the energy required from steam for this potentially new process was 475×10^5 kJ/hr. The high-pressure (HP) steam supplied this energy, and 29,000 kg/hr of HP steam was used in the heat exchangers. The energy liberated from this process was 336×10^5 kJ/hr, and the cooling water required to absorb this energy was 402×10^3 kg/hr.

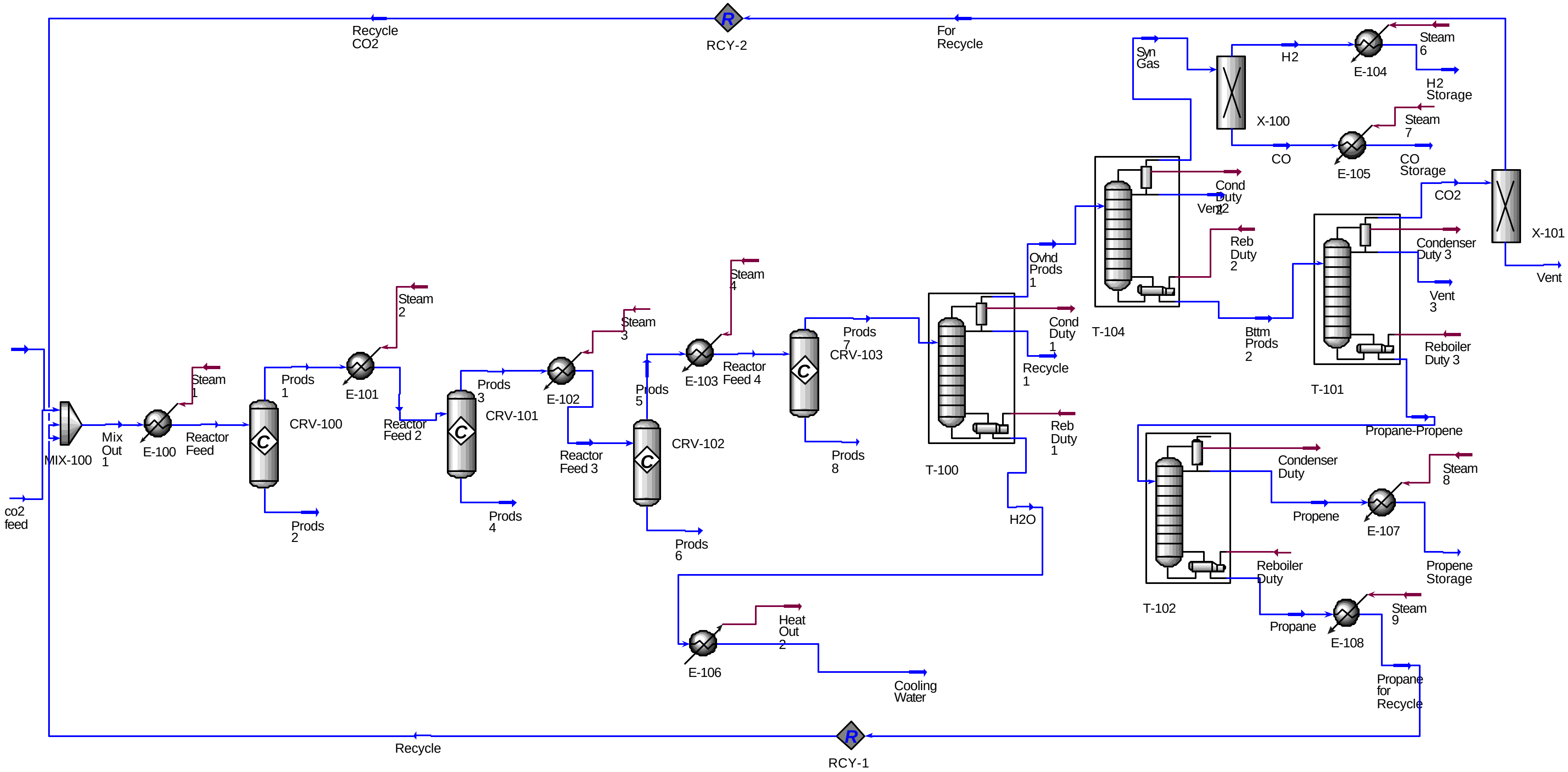


Figure 4.1. HYSYS Flow Sheet for the Production of Propylene described by Takahara, et al., 1998

Using the HYSYS flow sheet, the potential amount of CO_2 that could be utilized by this process was estimated to be 21,850 metric tons per year. The by-products of this process include carbon monoxide and hydrogen. The propylene produced was 99% pure.

The value added economic analysis gave a profit of 4.3 cents per kg of propylene. The economic data for this potentially new process is listed in Table 4.1. This value added economic model was based on a selling price of 0.16 cents per kg of propylene (C & EN, June 2003, p.15) as shown in Table 4.1. This potentially new process was included in the chemical complex.

Table 4.1. Economic Results for the HYSYS Simulated Propylene Production Process described by Takahara, et al., 1998.

Product/Raw Material	**Flow Rate from HYSYS Simulation (kg/hr)**	**Cost/Selling Price ($/kg)**	**Source**
Carbon Dioxide	2,493	0.003	Hertwig, T. A., Private Communication, 2003
Propane	5,028	0.163	C & EN, June 2003, p.15
Carbon Monoxide	1573	0.031	Appendix A
Propylene	4,784	0.24	C & EN, June 2003, p.15
Cooling Water	402×10^3	6.7×10^{-6}	Turton, et al., 1998
High Pressure Steam	29,000	0.00865	Turton, et al., 1998
Hydrogen	114	0.796	Appendix B
Value Added Profit	$ 207 / hr	4.3 cents/kg-propylene	

2) Propylene from Propane Dehydrogenation

A new propylene plant with a production capacity of 350,000 metric tons of propylene was built and operated by BASF Sonatrac PropanChem S.A., and it has started its trial operations at Tarragona, Spain (C & EN, June 2003, p.15). The process description was given in Chapter Three. Propylene was produced from propane dehydrogenation over a proprietary platinum catalyst (DeH-14). The conversion of propane per pass was 40% (C & EN, June 2003, p.15). The following reaction occurs in the reactor.

$$C_3H_8 \rightarrow C_3H_6 + H_2 \quad \Delta H^o = 124 \text{ kJ/mol}, \Delta G^o = 86 \text{ kJ/mol}$$

Although this process does not use CO_2 as a raw material, it was selected for HYSYS simulation as it provides a source for hydrogen needed for other processes in the chemical complex. As shown in HYSYS flow sheet, Figure 4.2, unreacted propane was recycled ensuring a 100% propane conversion. Hydrogen is a by-product of this process, and the purity of the produced propylene was 99.99%.

The plant capacity used in this simulation was 41,800 metric tons of propylene per year (4,767 kg/hr). This was based on Union Texas Ethylene Corporation plant, located in Geismar, LA, that produces propylene at a production capacity of 92 million lb/year (41,732 metric tons/year) (Louisiana Chemical & Petroleum Products List, 1998).

Based on the HYSYS flow sheet, the energy required for this process was 750 x 10^5 kJ/hr, and the HP steam required to supply this energy was 45,000 kg/hr. The energy liberated from this process was 609 x 10^5 kJ/hr. The cooling water required to absorb this heat was 728 x 10^3 kg/hr, as shown in Table 4.2.

Table 4.2. Economic Results for the HYSYS Simulated Propylene Production Process described in C & EN, June 2003, p.15.

Product/Raw Material	**Flow Rate from HYSYS Simulation (kg/hr)**	**Cost/Selling Price ($/kg)**	**Source**
Propane	4,996	0.163	C & EN, June 2003, p.15
Propylene	4,767	0.24	C & EN, June 2003, p.15
Hydrogen	229	0.796	Appendix B
High Pressure Steam	45,000	0.00865	Turton, et al., 1998
Cooling Water	728 x 10^3	6.7 x 10^{-6}	Turton, et al., 1998
Value Added Profit	$ 118 / hr	2.5 cents /kg-propylene	

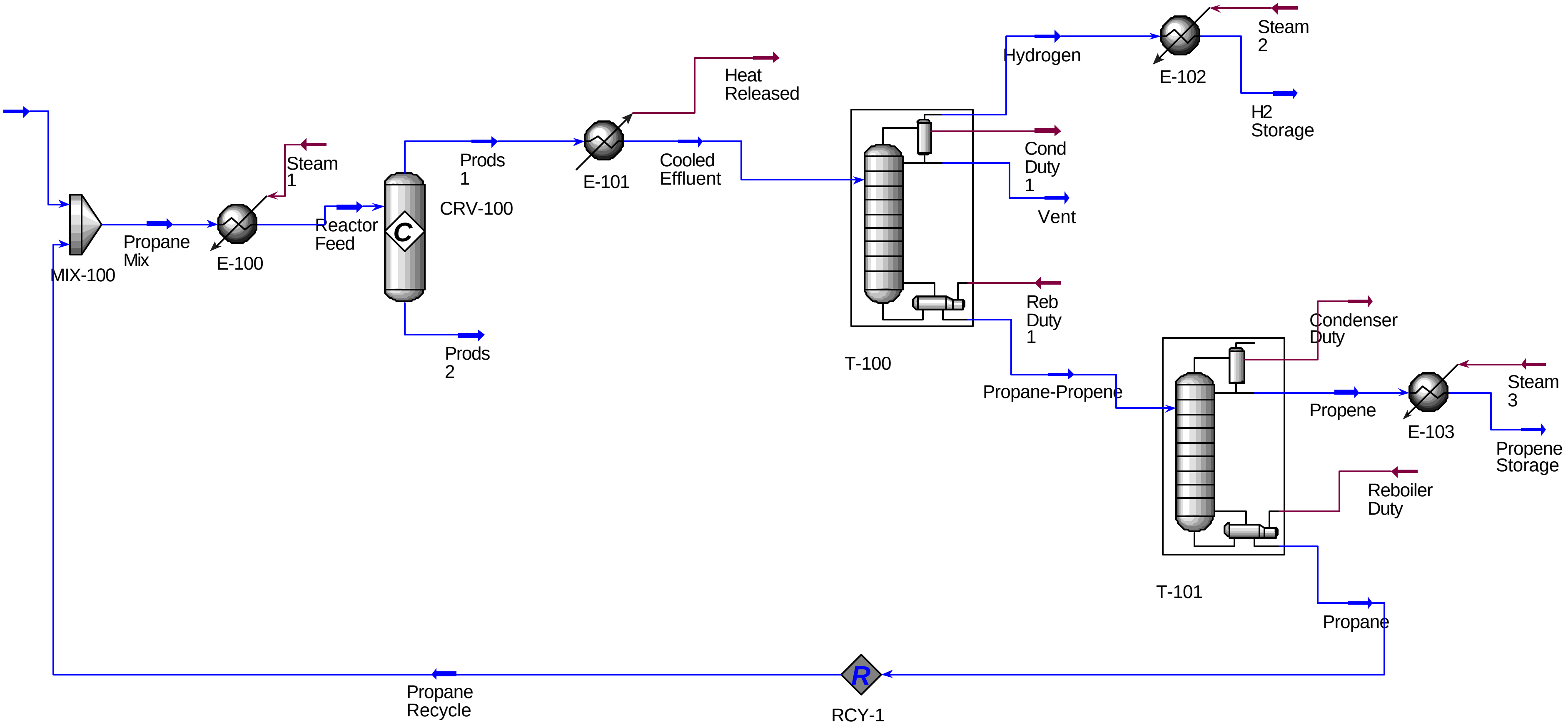


Figure 4.2. HYSYS Flow Sheet for the Production of Propylene described in C & EN, June 2003, p. 15.

The value added economic model gave a profit of 2.5 cents per kg propylene. The economic data for this process is listed in Table 4.2. This value added profit was based on a selling price of 0.16 cents per kg of propylene (C & EN, June 2003, p.15), as shown in Table 4.2. This potentially new process was included in the chemical complex.

D) Methanol Production

Five potentially new processes for the production of methanol were simulated using HYSYS. The results of these simulations are described below.

1) Methanol from CO_2 Hydrogenation over Cu(100) Catalyst

The experimental study described by Nerlov and Chokendorff, 1999, for the production of methanol through CO_2 hydrogenation over a Cu(100) catalyst was simulated using HYSYS. The following reaction occurs in the reactor.

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H^o = -49 \text{ kJ/mol}, \Delta G^o = 3 \text{ kJ/mol}$$

The HYSYS flow sheet for this potentially new process is shown in Figure 4.3. The methanol production capacity of this simulated process was 480,000 metric tons per year (54,760 kg/hr). This was based on Ashland Chemical Inc., a methanol plant located in Plaquemine, LA, and the production capacity of this plant is 160 million gallons per year (480,846 metric tons/year) (Louisiana Chemical & Petroleum Products List, 1998).

Nerlov and Chokendorff, 1999, did not report the conversion of carbon dioxide. The yield of methanol in the commercial process from synthesis gas is 61% (Wells, 1999). Therefore, a conversion of carbon dioxide that is equal that of the commercial process was used for this simulation. The unreacted carbon dioxide was recycled, and 100% conversion of carbon dioxide was achieved. The produced methanol was 99% pure.

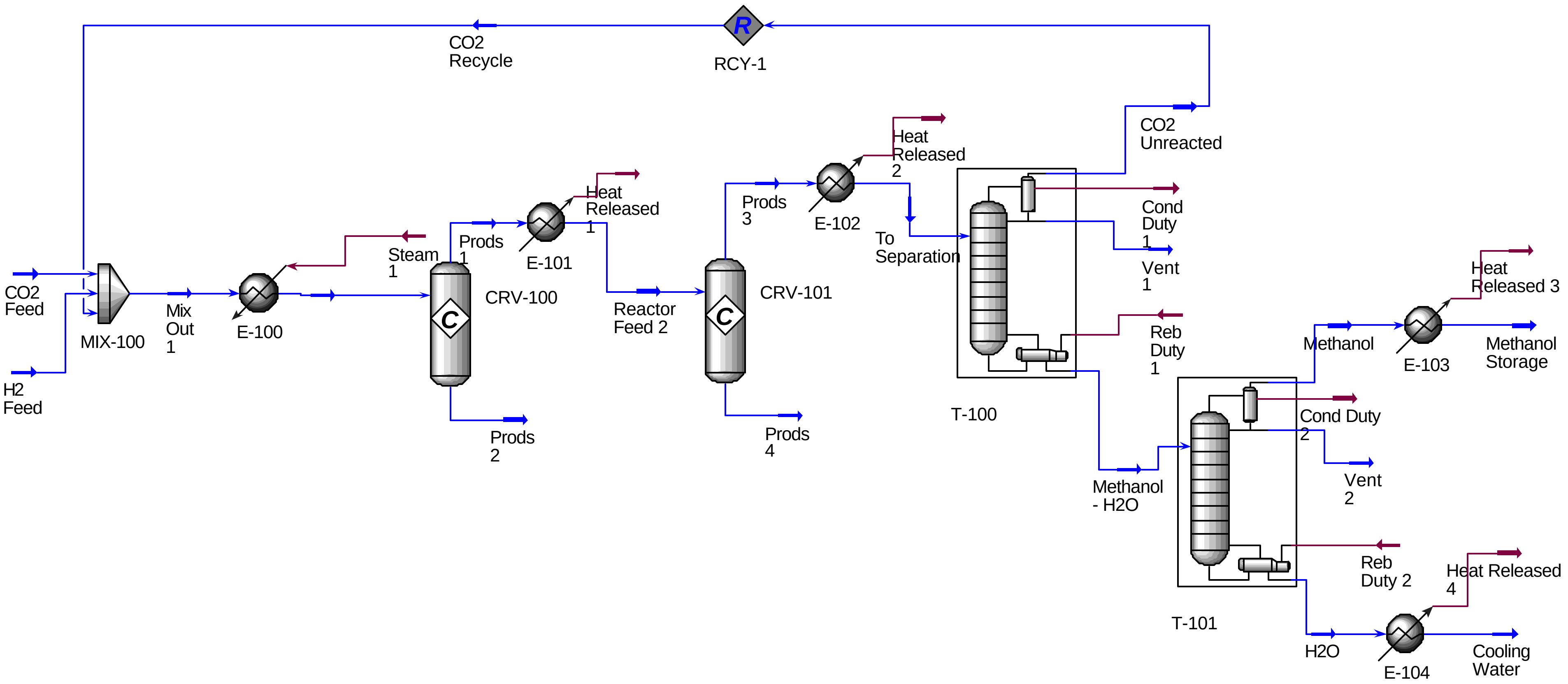


Figure 4.3. HYSYS Flow Sheet for the Production of Methanol described by Nerlov and Chokendorff, 1999.

Using HYSYS flow sheet, the energy required for this potentially new process was 1,289 x 10^6 kJ/hr. The HP steam required to supply this energy was 776 x 10^3 kg/hr. The energy liberated from this process was 1,518 x 10^6 kJ/hr. The cooling water required to absorb this energy was 1,816 x 10^4 kg/hr. The amount of CO_2 that can be utilized by this potentially new process was estimated to be 662,200 metric tons per year.

Based on the value added economic analysis, the model gave a profit of 2.8 cents per kg of methanol. This value added economic model was based on a selling price of 3 cents per kg of methanol (Chemical Market Reporter, 2003), as shown in Table 4.3. The economic data used in evaluating the value added economic model is listed in Table 4.3. This potentially new process was included in the chemical complex.

Table 4.3. Economic Results for the HYSYS Simulated Methanol Production Process by Nerlov and Chokendorff, 1999.

Product/Raw Material	**Flow Rate from HYSYS Simulation (kg/hr)**	**Cost/Selling Price ($/kg)**	**Source**
Carbon Dioxide	75,540	0.003	Hertwig, T. A., Private Communication, 2003
Hydrogen	10,380	0.796	Appendix B
Methanol	54,760	0.300	Chemical Market Reporter, 2003
Cooling Water	1,816 x 10^4	6.7 x 10^{-6}	Turton, et al., 1998
HP Steam	776 x 10^3	0.00865	Turton, et al., 1998
Value Added Profit	$ 1,536 / hr	2.8 cents/kg-methanol	

2) Methanol from CO_2 Hydrogenation over Cu - Zr Catalyst

The experimental study described by Toyir, et al., 1998, for the production of methanol by CO_2 hydrogenation was simulated using HYSYS. Raney Cu-Zr catalyst leached with aqueous solution of zincate (NaOH + ZnO) was used in this study. The author reported the formation of carbon monoxide along with methanol by CO_2 hydrogenation. The reactions involved in this study are:

$CO_2 + 3 H_2 \rightarrow CH_3OH + H_2O$ $\Delta H^o = -49$ kJ/mol, $\Delta G^o = 3$ kJ/mol
$CO_2 + H_2 \rightarrow CO + H_2O$ $\Delta H^o = 41$ kJ/mol, $\Delta G^o = 29$ kJ/mol

Toyir, et al., 1998 did not report the conversion of carbon dioxide. The yield of methanol in the commercial process from synthesis gas is 61% (Wells, 1999). Therefore, a conversion of CO_2 that is equal that of the commercial process was used for this simulation. The unreacted hydrogen was recycled, and a 100% conversion of CO_2 was achieved as shown in Figure 4.4. The produced methanol was 99% pure, CO was obtained as a by-product.

The methanol production capacity of this simulated process was 481,000 metric tons per year (54,870 kg/hr). This was based on Ashland Chemical Inc., a methanol plant located in Plaquemine, LA, and the production capacity of this plant is 160 million gallons per year (480,846 metric tons/year) (Louisiana Chemical & Petroleum Products List, 1998).

The HYSYS flow sheet for this potentially new process is shown in Figure 4.4. Using HYSYS flow sheet, the energy required for this process was 2,002 x 10^6 kJ/hr. The HP steam required to supply this energy was 1,205 x 10^3 kg/hr. Based on HYSYS flow sheet, the energy liberated from this process was 2,236 x 10^6 kJ/hr. The cooling water required to absorb this energy was 2,674 x 10^4 kg/hr. The amount of CO_2 that can be consumed by this process was estimated to be 1,327 x 10^3 metric tons per year.

Based on the value added economic model, a profit could not be obtained for this process. The value added economic model gave a loss of 7.6 cents per kg methanol, as shown in Table 4.4. This value added economic model was based on a selling price of 3 cents per kg of methanol (Chemical Market Reporter, 2003), as shown in Table 4.4. The economic data used for this process is listed in Table 4.4.

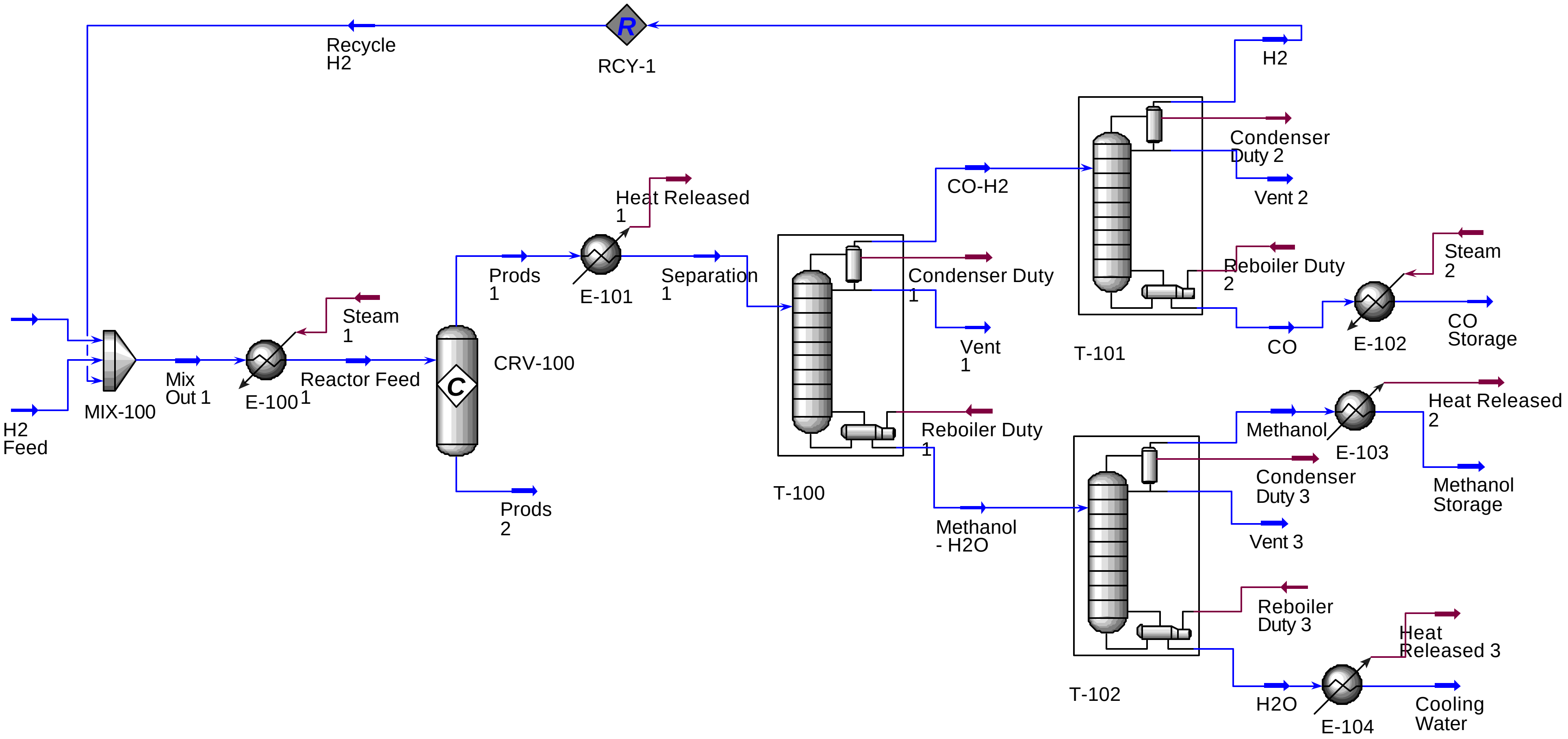


Figure 4.4. HYSYS Flow Sheet for the Production of Methanol described by Toyir, et al., 1998.

The loss obtained in the economic model was due to the reaction mechanism involved in this process. The process involves production of carbon monoxide along with methanol that consumed more hydrogen and carbon dioxide than other methanol production processes. Thus, the investment on raw materials increased leading to a loss obtained by the value added economic model. Since this process was not profitable based on the value added economic model, therefore, it will not be profitable with other costs included. Thus, this process was not included in the chemical complex.

Table 4.4. Economic Results for the HYSYS Simulated Methanol Production Process by Toyir, et al., 1998.

Product/Raw Material	**Flow Rate from HYSYS Simulation (kg/hr)**	**Cost/Selling Price ($/kg)**	**Source**
Carbon Dioxide	151,400	0.003	Hertwig, T. A., Private Communication, 2003
Hydrogen	13,870	0.796	Appendix B
Methanol	54,870	0.300	Chemical Market Reporter, 2003
Carbon Monoxide	48,180	0.031	Appendix A
Cooling Water	$2{,}674 \times 10^4$	6.7×10^{-6}	Turton, et al., 1998
High Pressure Steam	$1{,}205 \times 10^3$	0.00865	Turton, et al., 1998
Value Added Profit	$ - 4143 / hr	-7.6 cents/ kg-methanol	

3) Methanol from CO_2 Hydrogenation over $Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3$ Catalyst

The experimental study described by Ushikoshi, 2002, for the production of methanol by CO_2 hydrogenation was simulated using HYSYS. A multicomponent catalyst ($Cu/ZnO/ZrO_2/Al_2O_3/Ga_2O_3$) was used in this potentially new process. The CO_2 conversion per pass was 17% (Ushikoshi, 2002). The reactions involved in the reactor are:

$$CO_2 + 3\ H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H^o = -49\ kJ/mol,\ \Delta G^o = 3\ kJ/mol$$

$CO_2 + H_2 \rightarrow CO + H_2O$ $\Delta H^o = 41$ kJ/mol, $\Delta G^o = 29$ kJ/mol
$CO + 2H_2 \rightarrow CH_3OH$ $\Delta H^o = -90.5$ kJ/mol, $\Delta G^o = -25$ kJ/mol

The methanol production capacity of this simulated process was 479,800 metric tons per year (54,730 kg/hr). This was based on Ashland Chemical Inc., a methanol plant located in Plaquemine, LA, and the production capacity of this plant is 160 million gallons per year (480,846 metric tons/year) (Louisiana Chemical & Petroleum Products List, 1998). The purity of methanol produced was 99%, and carbon monoxide was obtained as by-product. The HYSYS flow sheet for this potentially new process is shown in Figure 4.5.

Using HYSYS flow sheet, the energy required for this process was 1,152 x 10^6 kJ/hr. The HP steam required to supply this energy was 693 x 10^3 kg/hr. The heat energy liberated from this process was 138 x 10^7 kJ/hr. The cooling water required to absorb this energy was 1,651 x 10^4 kg/hr. Using HYSYS flow sheet, the amount of CO_2 that can be consumed by this process was estimated to be 670,150 metric tons per year.

Table 4.5. Economic Results for the HYSYS Simulated Methanol Production Process by Ushikoshi, 2002.

Product/Raw Material	**Flow Rate from HYSYS Simulation (kg/hr)**	**Cost/Selling Price (\$/kg)**	**Source**
Carbon Dioxide	76,450	0.003	Hertwig, T. A., Private Communication, 2003
Hydrogen	10,420	0.796	Appendix B
Methanol	54,730	0.300	Chemical Market Reporter, 2003
Carbon Monoxide	585	0.031	Appendix A
HP Steam	693 x 10^3	0.00865	Turton, et al., 1998
Cooling Water	1,651 x 10^4	6.7 x 10^{-6}	Turton, et al., 1998
Value Added Profit	\$ 1,810 / h	3.3 cents/kg-methanol	

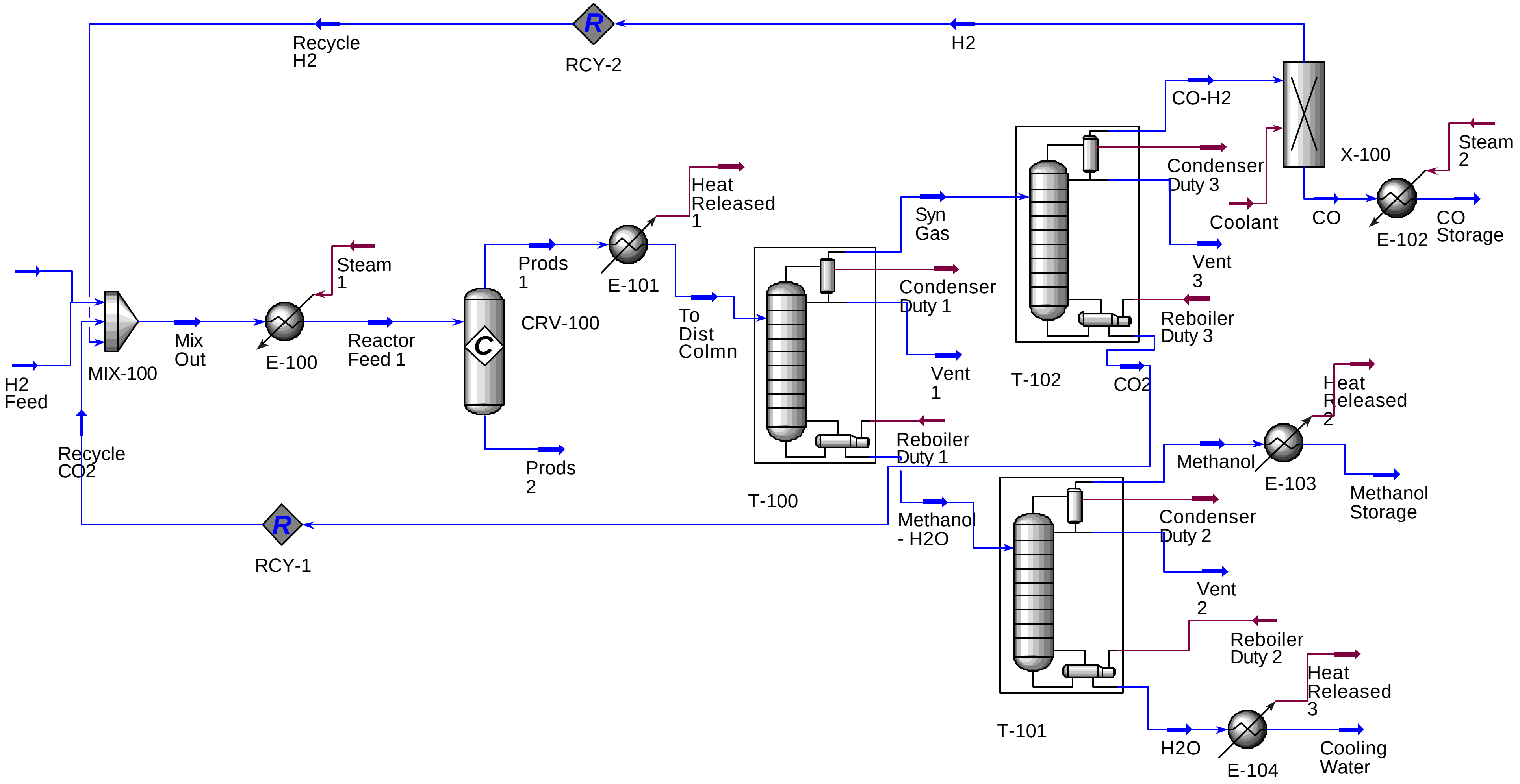


Figure 4.5. HYSYS Flow Sheet for the Production of Methanol described by Ushikoshi, 2002.

As shown in Table 4.5, the value added economic model gave a profit of 3.3 cents per kg methanol. This profit was based on a selling price of 3 cents per kg of methanol (Chemical Market Reporter, 2003). This potentially new process was included in the chemical complex.

4) Methanol from Hydrogenation over $Cu/ZnO/Cr_2O_3$ and CuNaY Zeolite Catalyst

The HYSYS flow sheet for the production of methanol by CO_2 hydrogenation based on the experimental study described by Jun, et al., 1998, is shown in Figure 4.6. This study uses a hybrid catalyst of $Cu/ZnO/Cr_2O_3$ and CuNaY zeolite. Small amount of dimethyl ether (DME) was co produced along with methanol. The conversion of CO_2 to CO was 10.21% and to oxygenates was 9.37% (Jun, et al., 1998). The selectivity of dimethyl ether in oxygenates was 36.7% (Jun, et al., 1998). Using the selectivity to DME in oxygenates and the total conversion to oxygenates, the specific conversion to DME was calculated to be 3.44%. Unreacted CO_2 and H_2 were recycled, thus the conversion was 100%, as shown in Figure 4.6. The following reactions occur in the reactor.

$CO_2 + H_2 \rightarrow CO + H_2O$ $\Delta H^o = 41$ kJ/mol, $\Delta G^o = 29$ kJ/mol
$CO + 2H_2 \rightarrow CH_3OH$ $\Delta H^o = -90.5$ kJ/mol, $\Delta G^o = -25$ kJ/mol
$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$ $\Delta H^o = -24$ kJ/mol, $\Delta G^o = -17$ kJ/mol

The methanol production capacity of this simulated process was 479,800 metric tons per year (54,700 kg.hr). This was based on Ashland Chemical Inc., a methanol plant located in Plaquemine, LA, and the production capacity of this plant is 160 million gallons per year (480,846 metric tons/year) (Louisiana Chemical & Petroleum Products List, 1998).

Using HYSYS flow sheet, the energy required for this process was $1{,}001 \times 10^6$ kJ/hr. The HP steam required to supply this energy was 602×10^3 kg/hr. The energy

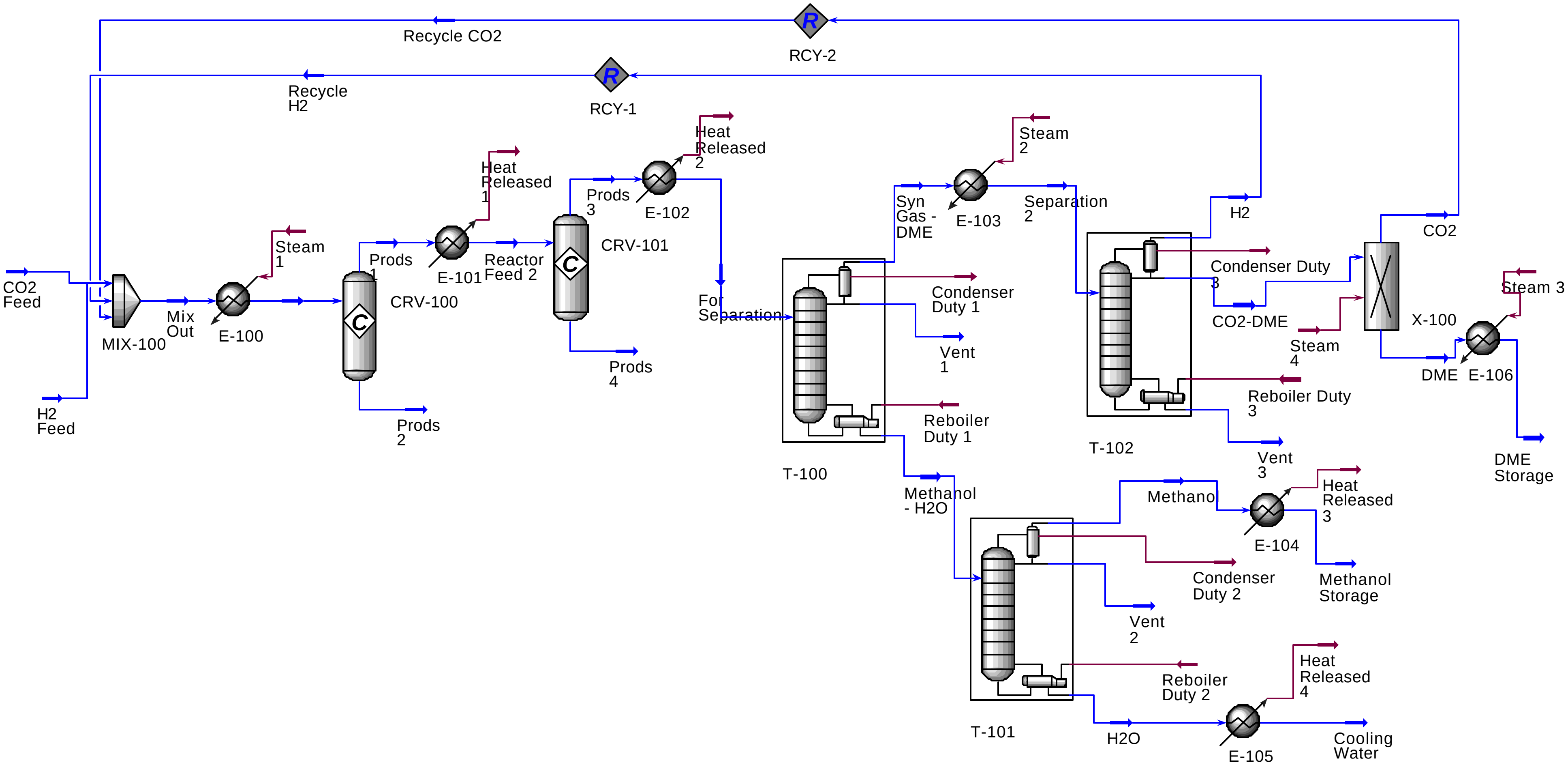


Figure 4.6. HYSYS Flow Sheet for the Production of Methanol described by Jun, et al., 1998.

liberated from this process was 1,237 x 10^6 kJ/hr. The cooling water required to absorb this energy was 1,480 x 10^5 kg/hr. The amount of CO_2 that can be utilized by this process was estimated to be 699,000 metric tons per year.

A value added economic analysis was evaluated for this process, and the model gave a profit of 7.6 cents per kg of methanol. This profit was based on a selling price of 3 cents per kg of methanol (Chemical Market Reporter, 2003), as shown in Table 4.6. The economic data used in the value added economic analysis for this process is listed in Table 4.6. This potentially new process was included in the chemical complex.

Table 4.6. Economic Results for the HYSYS Simulated Methanol Production Process by Jun, et al., 1998.

Product/Raw Material	**Flow Rate from HYSYS Simulation (kg/hr)**	**Cost/Selling Price ($/kg)**	**Source**
Carbon Dioxide	79,740	0.003	Hertwig, T. A., Private Communication, 2003
Hydrogen	10,940	0.796	Appendix B
Methanol	54,700	0.300	Chemical Market Reporter, 2003
Dimethyl Ether (DME)	2,102	0.946	
High Pressure Steam	602 x 10^3	0.00865	Turton, et al., 1998
Cooling Water	1,480 x 10^5	6.7 x 10^{-6}	Turton, et al., 1998
Value Added Profit	$ 4,143 / hr	7.6 cents/kg-methanol	

5) Methanol from Hydrogenation over Pd/SiO_2 Catalyst

The experimental study described by Bonivardi, et al., 1998, for the production of methanol by CO_2 hydrogenation over calcium promoted Pd/SiO_2 catalyst was simulated using HYSYS. The HYSYS flow sheet for this process is shown in Figure 4.7. Bonivardi, et al., 1998, did not report the conversion of carbon dioxide. The yield of methanol in the commercial process from synthesis gas is 61% (Wells, 1999). Therefore, a conversion of

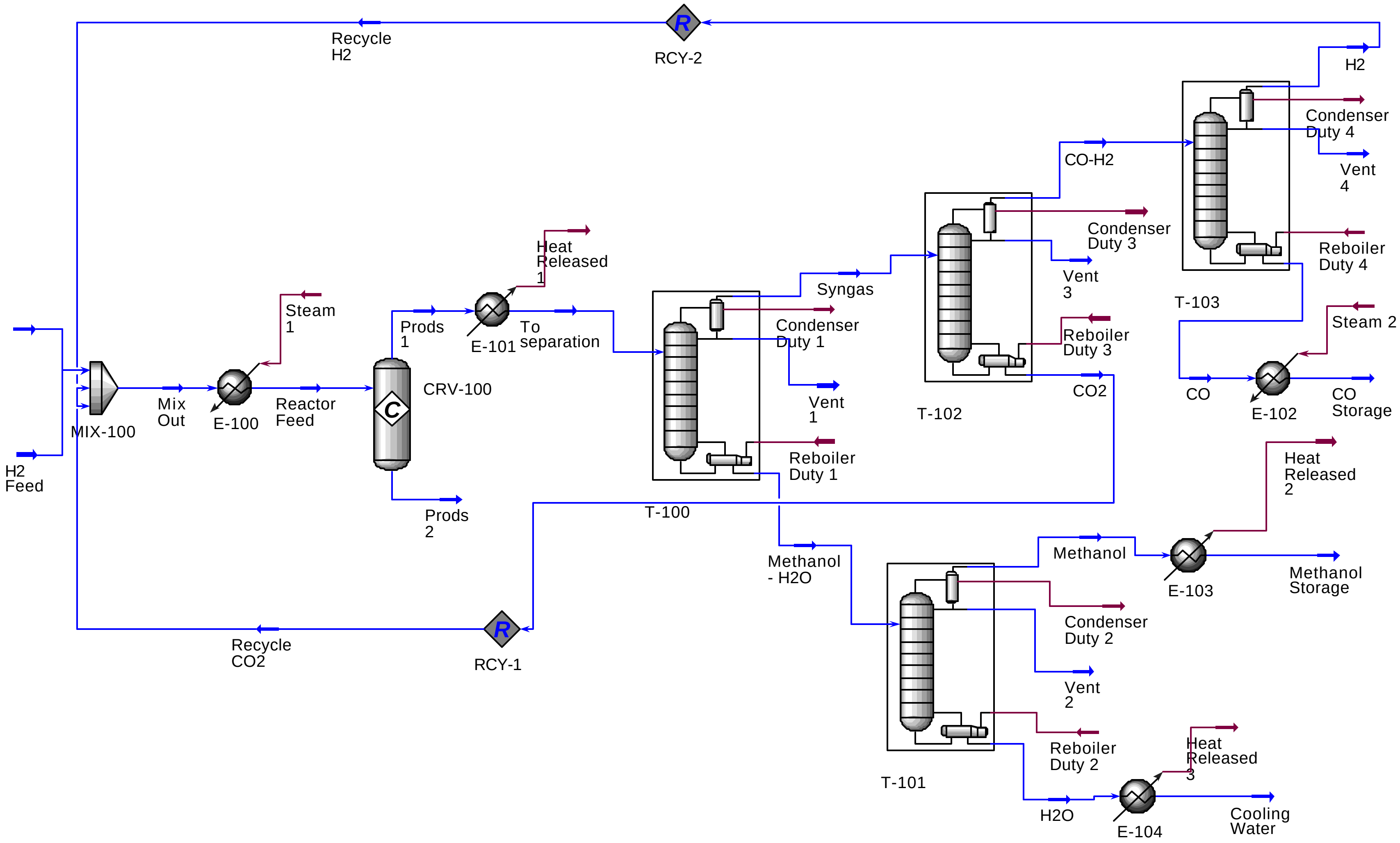


Figure 4.7. HYSYS Flow Sheet for the Production of Methanol described by Bonivardi, et al., 1998.

carbon dioxide equal to that of the commercial process was used for this simulation. Complete conversions of the raw materials were achieved, as the unreacted feed was recycled.

$CO_2 + H_2 \rightarrow CO + H_2O$ ΔHº = 41 kJ/mol, ΔGº = 29 kJ/mol
$CO + 2H_2 \rightarrow CH_3OH$ ΔHº = -90.5 kJ/mol, ΔGº = -25 kJ/mol

The methanol production capacity of this simulated process was 480,370 metric tons per year (54,800 kg/hr). This was based on Ashland Chemical Inc., a methanol plant located in Plaquemine, LA, and the production capacity of this plant is 160 million gallons per year (480,846 metric tons/year) (Louisiana Chemical & Petroleum Products List, 1998).

Using HYSYS flow sheet, the energy required for this process was 8,724 x 10^5 kJ/hr. The HP steam required to supply this energy was 525 x 10^3 kg/hr. The energy liberated from this process was 1,102 x 10^6 kJ/hr. The cooling water required to absorb this energy was 1,318 x 10^4 kg/hr. The amount of CO_2 that can be consumed by this plant was estimated to be 697,700 metric tons per year.

Table 4.7. Economic Results for the HYSYS Simulated Methanol Production Process by Bonivardi, et al., 1998.

Product/Raw Material	**Flow Rate from HYSYS Simulation (kg/hr)**	**Cost/Selling Price ($/kg)**	**Source**
Carbon Dioxide	79,590	0.003	Hertwig, T. A., Private Communication, 2003
Hydrogen	10,570	0.796	Appendix B
Methanol	54,800	0.300	Chemical Market Reporter, 2003
Carbon Monoxide	2,527	0.031	Appendix A
High Pressure Steam	525 x 10^3	0.00865	Turton, et al., 1998
Cooling Water	1,318 x 10^4	6.7 x 10^{-6}	Turton, et al., 1998
Value Added Profit	$ 3,234/ hr	5.9 cents/kg-methanol	

As shown in Table 4.7, the value added economic model of this plant gave a profit of 5.9 cents per kg of methanol. This economic model was based on a selling price of 3 cents per kg of methanol (Chemical Market Reporter, 2003). This potentially new process was included in the chemical complex.

6) Summary of Methanol Processes

In summary five new processes for the production of methanol were simulated using HYSYS. The results of the value added economic analyses of these processes are shown in Table 4.8.

Table 4.8. Results of the Value Added Economic Analyses of New Methanol Processes.

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
Methanol	CO_2 hydrogenation	-7.6	Toyir, et al., 1998

Based on the value added economic profit, the processes described by Nerlov and Chorkendorff, 1999, Ushikoshi, et al., 1998, Jun, et al., 1998, and Bonivardi, et al., 1998, were profitable. The reaction mechanisms involved in all of these processes were different from each other. Thus, these four new processes were included in the chemical complex. The value added economic analysis for the process described by Toyir, et al., 1998, gave a loss 7.6 cents per kg of methanol. Thus, this process was not included in the chemical complex.

E) Ethanol Production

Two potentially new processes for the production of ethanol were selected and simulated by HYSYS. The results of these simulations are given below. Ethanol and water form a minimum boiling azeotrope at a temperature of 351K, where the mixture contains 89 mol% ethanol (Moulijn, 2001). Starting with a mixture containing a lower proportion of ethanol, it is not possible to obtain a product richer in ethanol than 89%. The mixture could be separated with azeotropic distillation, where benzene is added to form a ternary azeotrope (Moulijn, 2001).

Using HYSYS flow sheet, it was observed that the separation of ethanol and water mixture beyond 90 mol% ethanol is energy intensive. Such a process requires high capital investment to meet the energy demands. Based on the value added economic analysis, a profit could not be obtained if ethanol was produced with purity greater than 90 mol%. Thus, the ethanol produced in these simulations was 90 mol% pure.

1) Ethanol from CO_2 Hydrogenation over Cu-Zn-Fe-K catalyst

The experimental study by Inui, 2002, for the production of ethanol by CO_2 hydrogenation over a Cu-Zn-Fe-K catalyst was simulated using HYSYS. The HYSYS flow sheet for this process is shown in Figure 4.8. The conversion of CO_2 per single pass was 21.2% (Inui, 2002). The unreacted CO_2 and H_2 were recycled, as shown in Figure 4.8. Thus, a total conversion of CO_2 was obtained. The following reaction occurs in this study.

$$2CO_2 + 6H_2 \rightarrow C_2H_5OH + 3H_2O \qquad \Delta H^o = -173 \text{ kJ/mol}, \Delta G^o = -65 \text{ kJ/mol}$$

The ethanol production capacity of the simulated plant was selected to be 104,700 metric tons per year (11, 950 kg/hr). This production capacity was based on Shepherd Oil, an ethanol plant located in Jennings, LA, and the production capacity of this plant is 36 million gallons of ethanol per year (107,500 metric tons/year)(Louisiana Chemical & Petroleum Products List, 1998). The ethanol produced in this process was 88% pure.

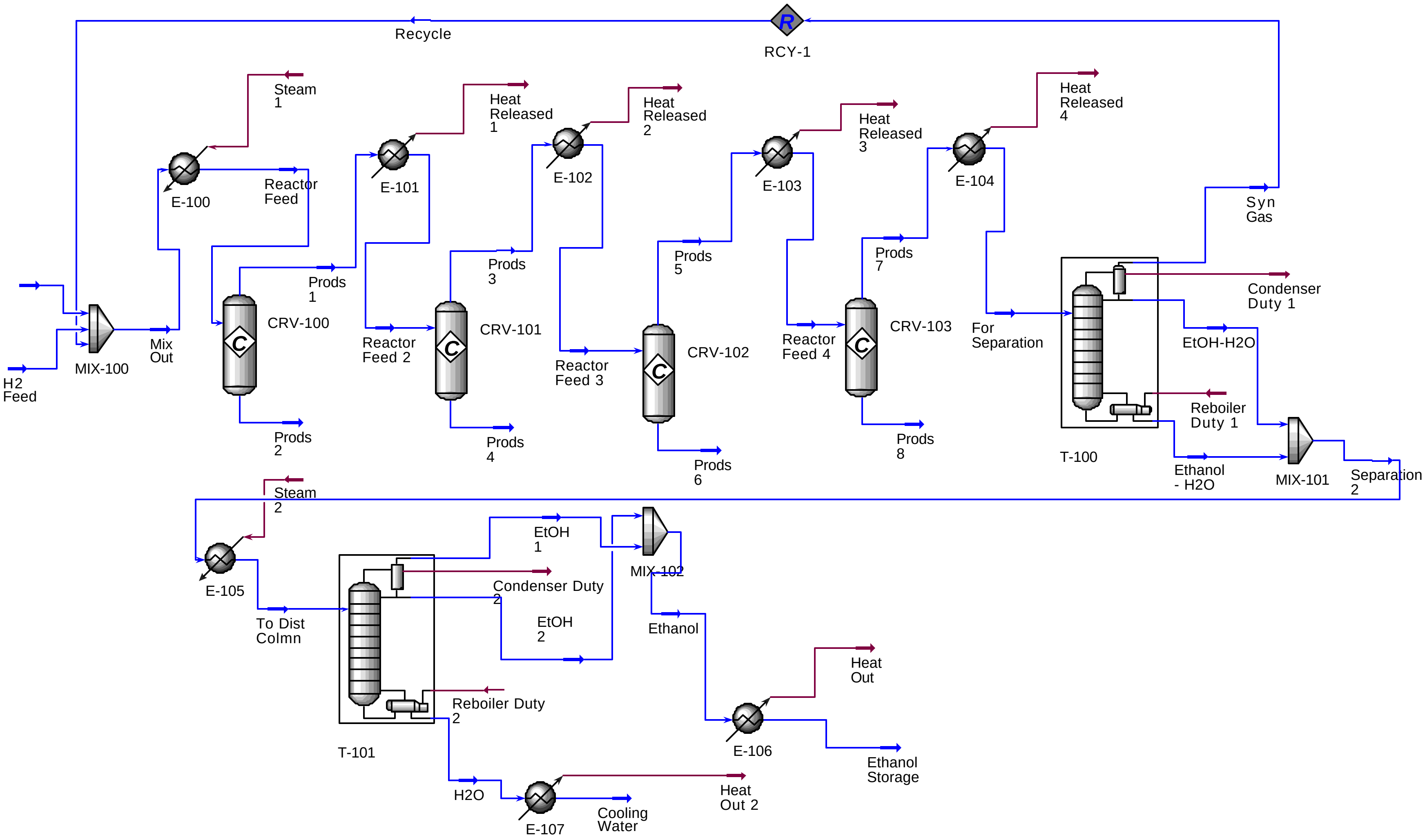


Figure 4.8. HYSYS Flow Sheet for the Production of Ethanol described by Inui, 2002.

Using HYSYS flow sheet, the energy required for this process was 276 x 10^6 kJ/hr. The HP steam required to supply this energy was 166 x 10^3 kg/hr, as shown in Table 4.9. The energy liberated from this process was 373 x 10^6 kJ/hr, and the cooling water required to absorb this heat was 446 x 10^4 kg/hr. Using the HYSYS flow sheet, the amount of CO_2 that can be utilized in this process was estimated to be 215,640 metric tons per year

The economic model for this process gave a profit of 31.6 cents per kg ethanol. The value added economic model was based on a selling price of 67 cents per kg of ethanol (Chemical Market Reporter, 2002), as shown in Table 4.9. The economic data used in this evaluation is listed in Table 4.9.

Table 4.9. Economic Results for the HYSYS Simulated Ethanol Production Process described by Inui, 2002.

Product/Raw Material	**Flow Rate from HYSYS Simulation (kg/hr)**	**Cost/Selling Price ($/kg)**	**Source**
Carbon Dioxide	24,600	0.003	Hertwig, T. A., Private Communication, 2003
Hydrogen	3,380	0.796	Appendix B
High Pressure Steam	166 x 10^3	0.00865	Turton, et al., 1998
Ethanol	11,950	0.670	Chemical Market Reporter, 2002
Cooling Water	446 x 10^4	6.7 x 10^{-6}	Turton, et al., 1998
Value Added Profit	$ 3774 / hr	31.6 cents/kg-ethanol	

2) Ethanol from CO_2 Hydrogenation over K/Cu-Zn-Fe-Cr oxide catalyst

The experimental study described by Higuchi, et al., 1998, for the production of ethanol by CO_2 hydrogenation over a K/Cu-Zn-Fe-Cr oxide catalyst was simulated using HYSYS. The conversion of CO_2 per pass was 35% (Higuchi, et al., 1998). As shown in Figure 4.9, the unreacted CO_2 and H_2 were recycled, and a total conversion of CO_2 was

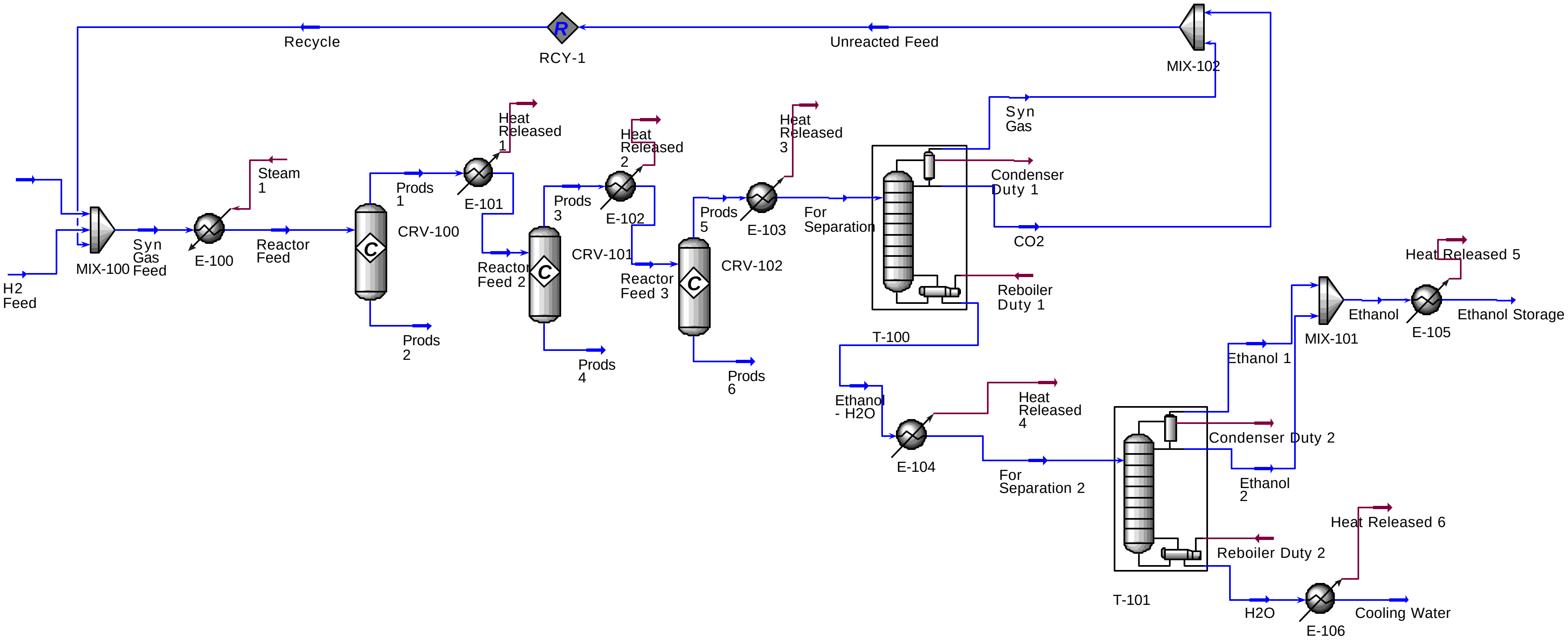


Figure 4.9. HYSYS Flow Sheet for the Production of Ethanol described by Higuchi, et al., 1998.

obtained. The HYSYS flow sheet for this study is shown in Figure 4.9. The following reaction occurs in the reactor.

$$2CO_2 + 6H_2 \rightarrow C_2H_5OH + 3H_2O \qquad \Delta H^o = -173 \text{ kJ/mol}, \Delta G^o = -65 \text{ kJ/mol}$$

The ethanol production capacity of the simulated plant was selected to be 103,700 metric tons of ethanol per year (11,830 kg/hr). This production capacity was based on Shepherd Oil, an ethanol plant located in Jennings, LA, and the production capacity of this plant is 36 million gallons of ethanol per year (107,500 metric tons/year)(Louisiana Chemical & Petroleum Products List, 1998). The ethanol produced in this process was 88% pure.

Using HYSYS flow sheet, the energy required for this potentially new process was 259 x 10^6 kJ/hr. The HP steam required to supply this energy was 156 x 10^3 kg/hr. The energy liberated from this process was 352 x 10^6 kJ/hr. The cooling water required to absorb this heat was 421 x 10^4 kg/hr, as shown in Table 4.10. Using HYSYS flow sheet, the amount of CO_2 that can be consumed by this process was estimated to be 205,640 metric tons per year.

Table 4.10. Economic Results for the HYSYS Simulated Ethanol Production Process described by and Higuchi, et al., 1998.

Product/Raw Material	**Flow Rate from HYSYS Simulation (kg/hr)**	**Cost/Selling Price ($/kg)**	**Source**
Carbon Dioxide	23,460	0.003	Hertwig, T. A., Private Communication, 2003
Hydrogen	3,224	0.796	Appendix B
High Pressure Steam	156 x 10^3	0.00865	Turton, et al., 1998
Ethanol	11,830	0.670	Chemical Market Reporter, 2002
Cooling Water	421 x 10^4	6.7 x 10^{-6}	Turton, et al., 1998
Value Added Profit	$ 3,914 / hr	33.1 cents/kg-ethanol	

A value added economic analysis was evaluated, and the model gave a profit of 33.1 cents per kg ethanol. This profit was based on a selling price of 67 cents per kg of ethanol (Chemical Market Reporter, 2002), as shown in Table 4.10. The data used for this economic evaluation is listed in Table 4.10.

3) Comparison of Ethanol Processes

The two processes simulated for ethanol production were similar to each other, and only one process was selected to integrate into the chemical complex. The value added economic model for the experimental study described by Inui, 2002, gave a profit of 31.6 cents per kg of ethanol. The economic model for the study described by Higuchi, et al., 1998, gave a profit of 33.1 cents per kg of ethanol. The best process based on the value added economic profit was selected. Thus, the potentially new process described by Higuchi, et al., 1998, was included in the chemical complex.

F) Dimethyl Ether Production

One potentially new process for the production of dimethyl ether (DME) was simulated using HYSYS. The results of this simulated process are given below.

1) Dimethyl Ether from CO_2 Hydrogenation

The experimental study described by Jun, et al., 2002, for the production of dimethyl ether (DME) by CO_2 hydrogenation was simulated using HYSYS. A γ-Al_2O_3 modified with 1% silica was used as catalyst. The conversion of methanol observed was 70% at 523 K (Jun, et al., 2002). Total conversion of reactants was achieved by the recycle. The by-products of this process include CO and methanol. The DME produced was 99.1% pure, and that of by-products methanol and CO were 99% and 100% pure respectively. The following reactions occur in the reactor.

$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ $\Delta H^o = -49$ kJ/mol, $\Delta G^o = 3.5$ kJ/mol
$CO_2 + H_2 \rightarrow CO + H_2O$ $\Delta H^o = 41$ kJ/mol, $\Delta G^o = 29$ kJ/mol
$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$ $\Delta H^o = -24$ kJ/mol, $\Delta G^o = -17$ kJ/mol

A production capacity for DME was not available in the Louisiana Chemical & Petroleum Products List, 1998. Therefore, a typical production capacity of 100 million pounds per year (45,360 metric tons/year) was taken as a basis. The DME production capacity of the simulated plant was selected to be 45,840 metric tons per year (5,230 kg/hr).

The HYSYS flow sheet for this process is shown in Figure 4.10. Using HYSYS flow sheet, the energy required for this process was 357×10^5 kJ/hr. The HP steam required to supply this energy was 21×10^3 kg/hr, as shown in Table 4.11. The energy liberated from this process was 679×10^5 kJ/hr. The cooling water required to absorb this energy was 812×10^3 kg/hr. The amount of CO_2 that could be utilized by this process was estimated to be 156,740 metric tons per year.

Table 4.11. Economic Data used for the HYSYS Simulated DME Production Process described by Jun, et al., 2002.

Product/Raw Material	**Flow Rate from HYSYS Simulation (kg/hr)**	**Cost/Selling Price ($/kg)**	**Source**
Carbon Dioxide	17,880	0.003	Hertwig, T. A., Private Communication, 2003
Hydrogen	1,839	0.796	Appendix B
High Pressure Steam	21×10^3	0.00865	Turton, et al., 1998
Carbon Monoxide	4,258	0.031	Appendix A
Dimethyl Ether (DME)	5,230	0.946	www.che.cemr.wvu.edu/publications/projects/dimethyl/dme-b.pdf
Methanol	891	0.300	Chemical Market Reporter, 2003
Cooling Water	812×10^3	6.7×10^{-6}	Turton, et al., 1998
Value Added Profit	$ 3,642 / hr	69.6 cents/kg-DME	

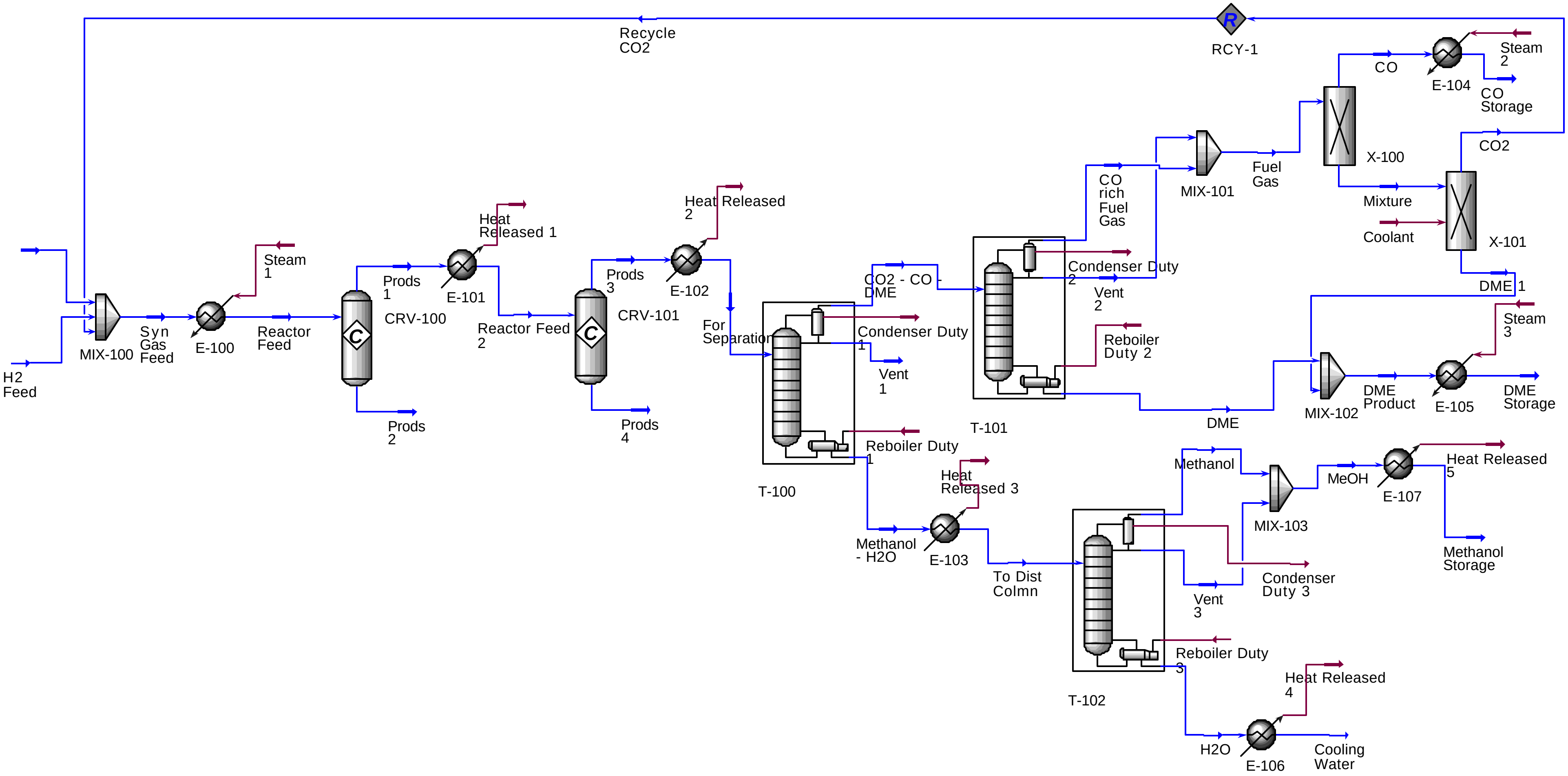


Figure 4.10. HYSYS Flow Sheet for the Production of DME described by Jun, et al., 2002.

The value added economic analysis of this process gave a profit of 69.6 cents per kg DME. The economic model was based on a selling price of 94.6 cents per kg of DME, as shown in Table 4.11. The economic data used for this process is shown in Table 4.11. This potentially new process was included in the chemical complex.

G) Formic Acid Production

One potentially new process for the production of formic acid was simulated using HYSYS. The results of this simulation are given below.

1) Formic Acid from CO_2 Hydrogenation

The experimental study described by Dinjus, 1998, for the production of formic acid by CO_2 hydrogenation was simulated using HYSYS. Wilkinson's catalyst [ClRh(TPPTS)$_3$] was used in this study. The HYSYS flow sheet for this process is shown in Figure 4.11. The unreacted hydrogen and CO_2 were recycled, and a total conversion of the reactants was achieved. Formic acid with 100% purity was produced. The following reaction occurs in the reactor.

$$CO_2\,(g) + H_2\,(g) \rightarrow HCOOH\,(l) \qquad \Delta H^o = -31\ \text{kJ/mol},\ \Delta G^o = 33\ \text{kJ/mol}$$

A production capacity for formic acid was not available in the Louisiana Chemical & Petroleum Products List, 1998. However, typical production capacities of formic acid ranged from 6,000 to 150,000 tons per year (Wells, 1999). Therefore, an average of the production capacity range specified above was used as a basis for the HYSYS simulation. Thus, the production of 78,000 metric tons of formic acid per year was taken as basis for the simulated plant. Using this production capacity as a basis, the formic acid production capacity of this simulated plant was selected to be 77,950 metric tons per year (8,892 kg/hr).

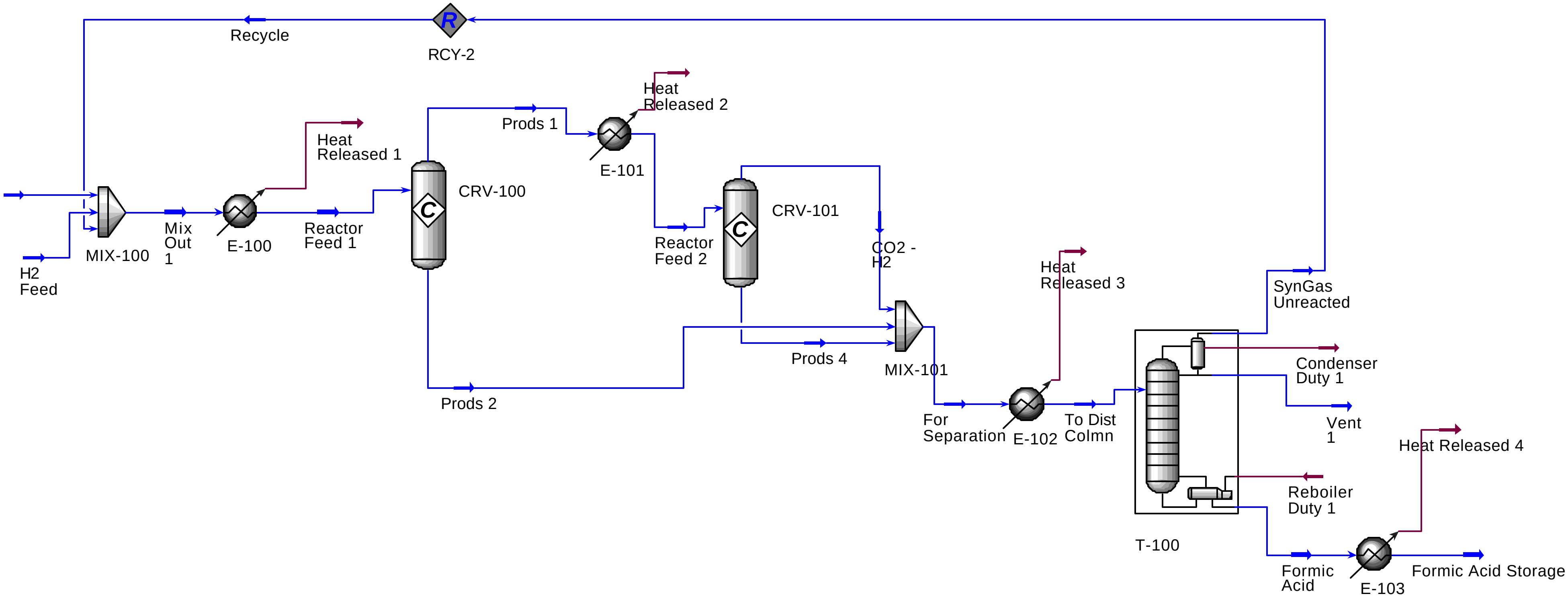


Figure 4.11. HYSYS Flow Sheet for the Production of Formic Acid described by Dinjus, 1998.

Based on the HYSYS flow sheet, the energy required for this process was 586 x 10^4 kJ/hr. The HP steam required to supply this energy was 3.5 x 10^3 kg/hr, as shown in Figure 4.11. Using HYSYS flow sheet, the energy liberated from this process was 762 x 10^4 kJ/hr. The cooling water required to absorb this heat was 91 x 10^3 kg/hr. The amount of CO_2 that can be consumed by this process was estimated to be 74,560 metric tons per year.

The value added economic model for this process gave a profit of 64.9 cents per kg of formic acid. This profit was based on a selling price of 69 cents per kg of formic acid (Chemical Market Reporter, 2002), as shown in Table 4.12. The data used for the economic analysis is shown in Table 4.12. This potentially new process was included in the chemical complex.

Table 4.12. Economic Results for the HYSYS Simulated Process for the Production of Formic Acid described by Dinjus, 1998.

Product/Raw Material	**Flow Rate from HYSYS Simulation (kg/hr)**	**Cost/Selling Price ($/kg)**	**Source**
Carbon Dioxide	8,506	0.003	Hertwig, T. A., Private Communication, 2003
Hydrogen	390	0.796	Appendix B
Formic Acid	8,892	0.690	Chemical Market Reporter, April 1, 2002
High Pressure Steam	3.5 x 10^3	0.00865	Turton, et al., 1998
Cooling Water	91 x 10^3	6.7 x 10^{-6}	Turton, et al., 1998
Value Added Profit	$ 5,769/ hr	64.9 cents/kg-formic acid	

H) Acetic Acid Synthesis

One potentially new process for the production of acetic acid was simulated using HYSYS. The results of this simulated plant are given below.

1) Acetic Acid from Methane and CO_2

The experimental study for the production of acetic acid described by Taniguchi, et al., 1998, was simulated using HYSYS. $VO(acac)_2$ (acac: acetylacetonate) was used as a catalyst. The HYSYS flow sheet for this process is shown in Figure 4.12. The acetic acid yield based on CH_4 was 97% (Taniguchi, et al., 1998). As shown in Figure 4.12, the unreacted methane and CO_2 were recycled. Thus, a total conversion of the reactants was achieved. Acetic acid with 100% purity was produced. Acetic acid was produced according to the following reaction.

$$CH_4 + CO_2 \rightarrow CH_3COOH \qquad \Delta H^o = 36 \text{ kJ/mol}, \Delta G^o = 71 \text{ kJ/mol}$$

The production capacity of this simulated plant was selected to be 8,175 metric tons/year (933 kg/hr). This was based on Union Carbide Corporation, an acetic acid plant located in Hahnville, LA, and the production capacity of this plant is 18 million lb/year (8,165 metric tons/year) (Louisiana Chemical & Petroleum Products List, 1998).

Based on the HYSYS flow sheet, the energy required for this process was estimated to be 1,273 x 10^3 kJ/hr. The HP steam required to provide this energy was 766 kg/hr, as shown in Table 4.13. Using HYSYS flow sheet, the heat energy liberated from this process was 1,148 x 10^3 kJ/hr, and the cooling water required to absorb this heat was 13,730 kg/hr. The amount of CO_2 that can be consumed by this potentially new process was estimated to be 6,005 metric tons of CO_2 per year.

As shown in Table 4.13, the value added economic model for this process gave a profit of 97.9 cents per kg acetic acid. This profit was based on a selling price of 103 cents per kg of acetic acid (Chemical Market Reporter, 2002. This potentially new process was included in the chemical complex.

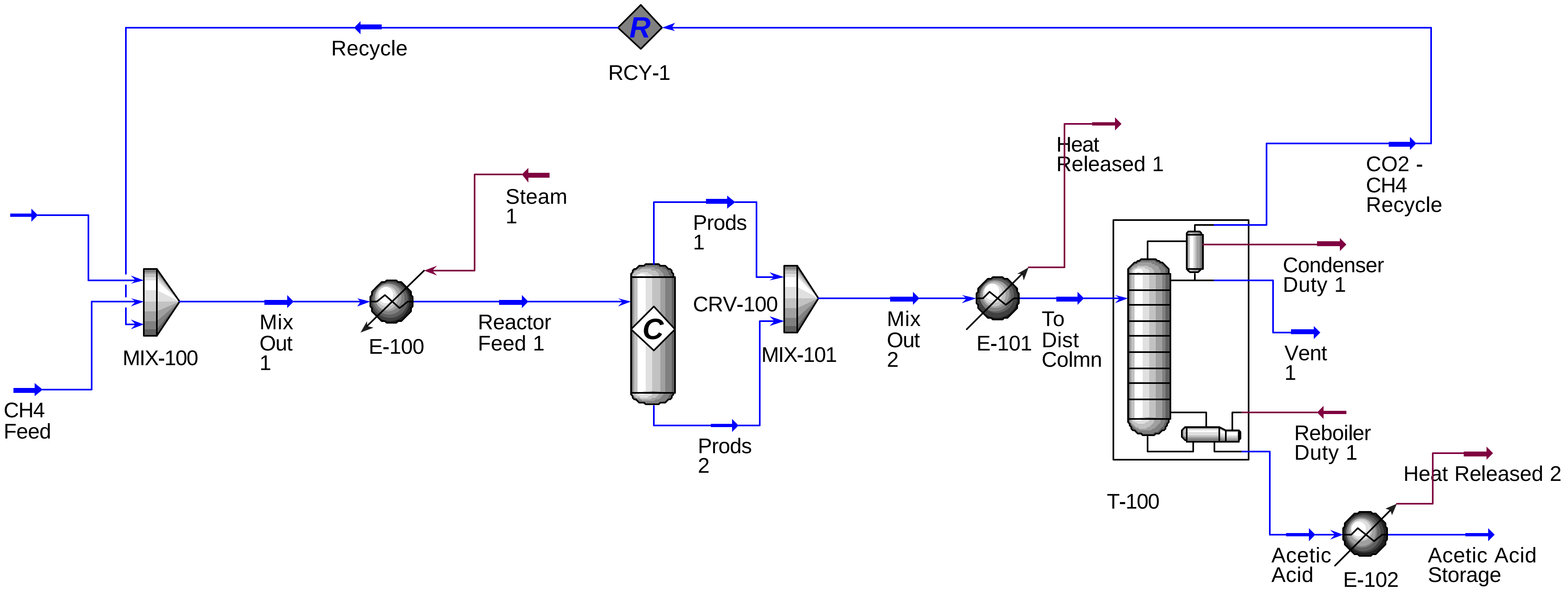


Figure 4.12. HYSYS Flow Sheet for the Production of Acetic Acid described by Taniguchi, et al., 1998.

Table 4.13. Economic Results for the HYSYS Simulated Process for the Production of Acetic Acid described by Taniguchi, et al., 1998.

Product/Raw Material	**Flow Rate from HYSYS Simulation (kg/hr)**	**Cost/Selling Price ($/kg)**	**Source**
Carbon Dioxide	685	0.003	Hertwig, T. A., Private Communication, 2003
Methane	249	0.172	http://www.repartners.org/renewables/recosts.htm
Acetic Acid	933	1.034	Chemical Market Reporter, 2002
High Pressure Steam	766	0.00865	Turton, et al., 1998
Cooling Water	13,730	6.7×10^{-6}	Turton, et al., 1998
Value Added Profit	$ 913 / hr	97.9 cents/kg-acetic acid	

I) Styrene Production

Two potentially new processes for styrene production were simulated using HYSYS. The results of these simulations are given below.

1) Styrene from Dehydrogenation over Vanadium Catalyst

The experimental study described by Sakurai, et al., 2000, for the production of styrene through dehydrogenation of ethylbenzene was simulated using HYSYS. Vanadium oxide loaded with MgO (V/MgO-100A) was used as a catalyst. Styrene produced in this process was 99.8% pure. Carbon monoxide with 100% purity was obtained as a by-product. The conversion of ethylbenzene was 59.1% per pass (Sakurai, et al., 2000). Complete conversion was achieved through recycling of unreacted CO_2 and ethylbenzene. The HYSYS flow sheet for this process is shown in Figure 4.13. The following reaction occurs in the reactor.

$C_6H_5C_2H_5 + CO_2 \rightarrow C_6H_5C_2H_3 + CO + H_2O$ $\Delta H^o = 159$ kJ/mol, $\Delta G^o = 112$ kJ/mol

The production capacity of this simulated process was selected to be 363,250 metric tons per year (41,440 kg/hr). This was based on Deltech Corporation, a styrene

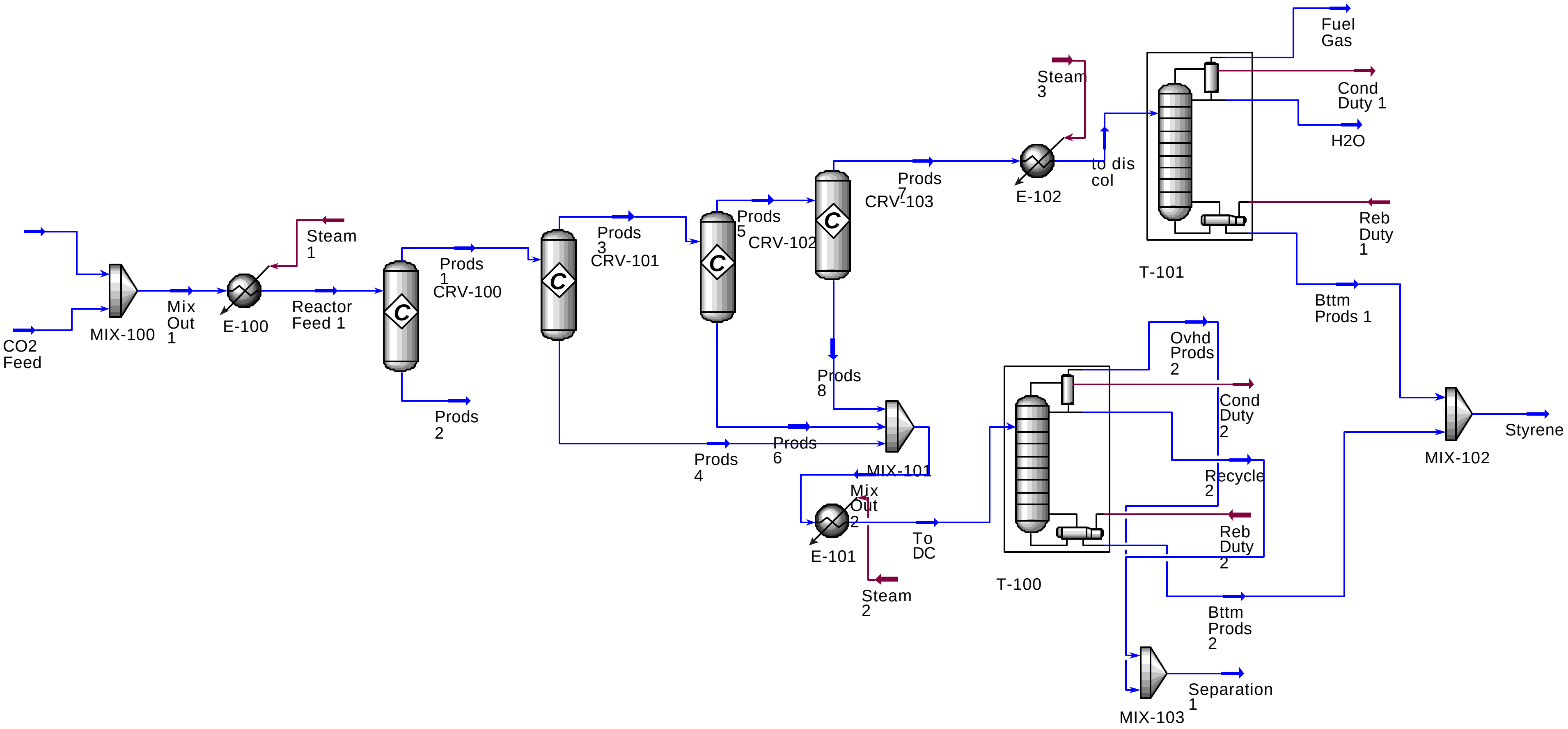


Figure 4.13. HYSYS Flow Sheet for the Production of Styrene described by Sakurai, et al., 2000.

plant located in Baton Rouge, LA, and the production capacity of this plant was 800 million pounds per year (362,880 metric tons/year) (Louisiana Chemical & Petroleum Products List, 1998).

Using HYSYS flow sheet, the energy required for this process was 832 x 10^6 kJ/hr. The HP steam required for supplying this energy was 501 x 10^3 kg/hr, as shown in Figure 4.13. The energy liberated from this process was 7,872 x 10^5 kJ/hr. The cooling water required for this process was 942 x 10^4 kg/hr. The amount of CO_2 that can be consumed by this process was estimated to be 153,450 metric tons CO_2 per year.

The economic model gave a profit of 4.5 cents per kg styrene. This was based on a selling price of 70.5 cents per kg of styrene (Chemical Market Reporter, 2002), as shown in Table 4.14. The data used for economic analysis is listed in Table 4.14.

Table 4.14. Economic Results for the HYSYS Simulated Styrene Production Process described by Sakurai, et al., 2000.

Product/Raw Material	**Flow Rate from HYSYS Simulation (kg/hr)**	**Cost/Selling Price (\$/kg)**	**Source**
Carbon Dioxide	17,505	0.003	Hertwig, T. A., Private Communication, 2003
Ethylbenzene	42,220	0.551	Chemical Market Reporter, 2002
High Pressure Steam	501 x 10^3	0.00865	Turton, et al., 1998
Carbon Monoxide	11,140	0.031	Appendix A
Styrene	41,440	0.705	Chemical Market Reporter, 2002
Cooling Water	942 x 10^4	6.7 x 10^{-6}	Turton, et al., 1998
Value Added Profit	\$ 1,845 / hr	4.5 cents/kg-styrene	

2) Styrene from Dehydrogenation over Fe/Ca/Al oxides Catalyst

Mimura, et al., 1998, described another experimental study for the production of styrene through dehydrogenation of ethylbenzene using carbon dioxide over a Fe/Ca/Al oxides catalyst. This study was simulated using HYSYS, and the HYSYS flow sheet for this process is shown in Figure 4.14. Carbon monoxide was obtained as a by-product. Styrene produced and the by-product CO were pure. The yield of styrene was 70%, and the selectivity to styrene was 100% (Mimura, et al., 1998). Thus, the conversion of ethylbenzene per pass was essentially 70%. Styrene was produced according to the following reaction.

$C_6H_5C_2H_5 + CO_2 \rightarrow C_6H_5C_2H_3 + CO + H_2O$ $\Delta H^o = 159$ kJ/mol, $\Delta G^o = 112$ kJ/mol

The capacity of this simulated process was selected to be 362,240 metric tons/year (41,320 kg/hr). This was based on Deltech Corporation, a styrene plant located in Baton Rouge, LA, and the production capacity of this plant was 800 million lb/year (362,880 metric tons/year) (Louisiana Chemical & Petroleum Products List, 1998).

Using the HYSYS flow sheet, the energy required for this process was 323×10^6 kJ/hr. The HP steam required to supply this energy was 194×10^3 kg/hr, as shown in Table 4.15. The energy liberated from this process was 277×10^6 kJ/hr, and the cooling water required to absorb this energy was 331×10^4 kg/hr. The amount of CO_2 that could be utilized by this process was estimated to be 153,100 metric tons per year.

Table 4.15. Economic Results for the HYSYS Simulated Styrene Production Process described by Mimura, et al., 1998.

Product/Raw Material	**Flow Rate from HYSYS Simulation (kg/hr)**	**Cost/Selling Price ($/kg)**	**Source**
Carbon Dioxide	17,460	0.003	Hertwig, T. A., Private Communication, 2003
Ethylbenzene	42,120	0.551	Chemical Market Reporter, 2002
High Pressure Steam	194×10^3	0.00865	Turton, et al., 1998
Carbon Monoxide	11,110	0.031	Appendix A
Styrene	41,320	0.705	Chemical Market Reporter, 2002
Cooling Water	331×10^4	6.7×10^{-6}	Turton, et al., 1998
Value Added Profit	$ 4,515 / hr	10.9 cents/kg-styrene	

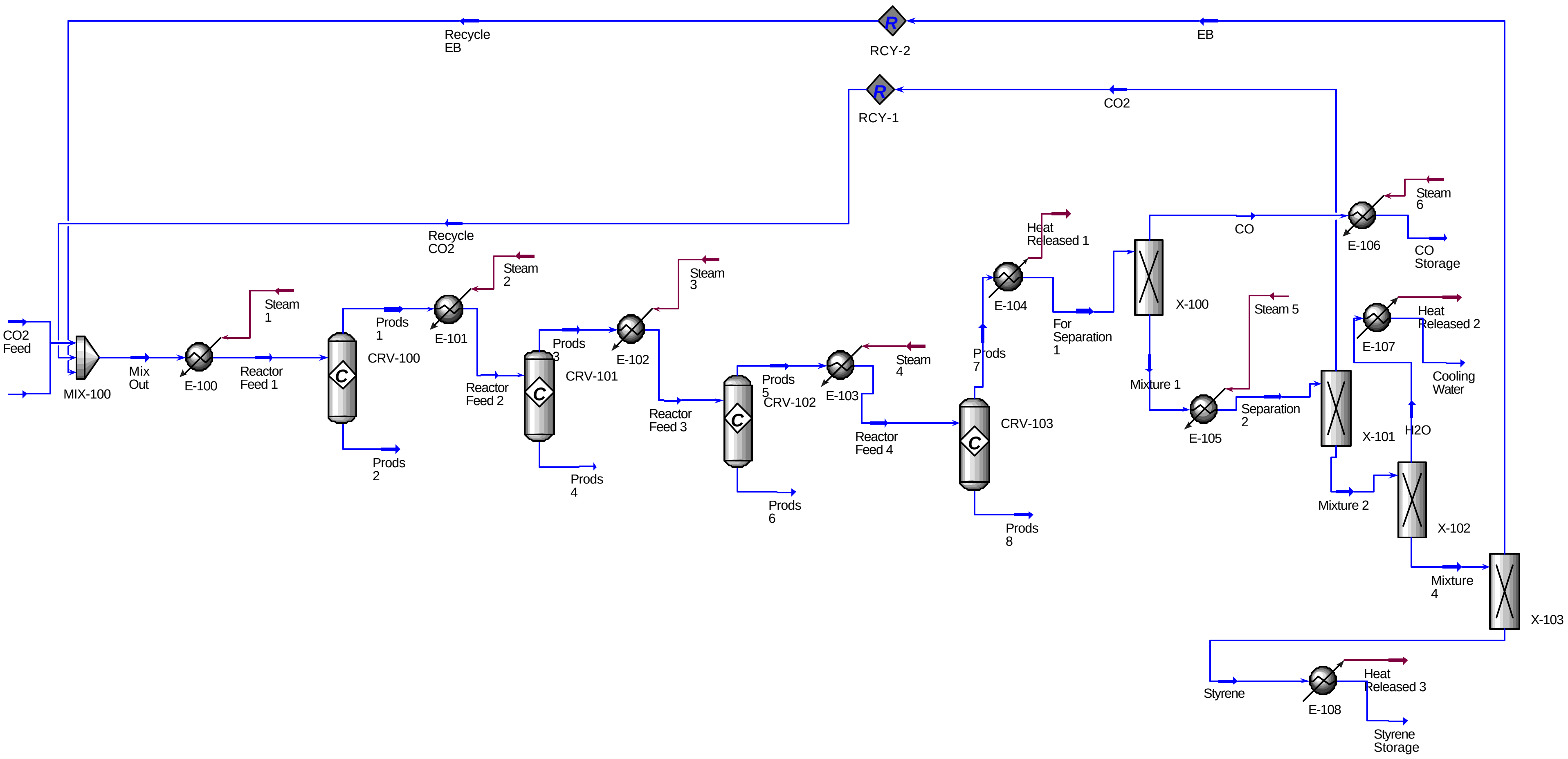


Figure 4.14. HYSYS Flow Sheet for the Production of Styrene described by Mimura, et al., 1998.

A value added economic analysis was evaluated, and the model gave a profit of 10.9 cents per kg styrene. This economic model was based on a selling price of 55 cents per kg of styrene (Chemical Market Reporter, 2002), as shown in Table 4.15.

3) Comparison of Styrene Plants

The two processes simulated for styrene production were similar to each other, and only one process was selected to integrate in the chemical complex. Based on the value added economic analysis, the two experimental studies were compared to each other. The study described by Sakurai, et al., 2000, gave a profit of 4.5 cents per kg of styrene, whereas the study described by Mimura, et al., 1998, gave a profit of 10.9 cents per kg of styrene. The best process based on the value added economic profit was selected. Thus, the potentially new process described by Mimura, et al., 1998, was included in the chemical complex.

J) Methylamines Production

One potentially new process for the production of methylamines was simulated using HYSYS. The results of this simulation are given below.

1) Methylamines from CO_2, H_2 and NH_3 over Cu/Al_2O_3 catalyst

Arakawa, 1998, described an experimental study for the production of methylamines from a mixture of CO_2, H_2, and NH_3. The catalyst used in this study was 51 wt% Cu/Al_2O_3. Mono- and di-methylamines (MMA & DMA) were produced with the by-product CO. This study was simulated using HYSYS, and the flow sheet is shown in Figure 4.15. The following reactions occur in this study.

$CO_2 + H_2 \rightarrow CO + H_2O$ $\Delta H^o = 41$ kJ/mol, $\Delta G^o = 29$ kJ/mol
$CO + 2H_2 \rightarrow CH_3OH$ $\Delta H^o = -90.5$ kJ/mol, $\Delta G^o = -25$ kJ/mol
$CH_3OH + NH_3 \rightarrow CH_3NH_2 + H_2O$ $\Delta H^o = -17$ kJ/mol, $\Delta G^o = -17$ kJ/mol
$CH_3OH + CH_3NH_2 \rightarrow (CH_3)_2NH + H_2O$ $\Delta H^o = -37$ kJ/mol, $\Delta G^o = -30$ kJ/mol

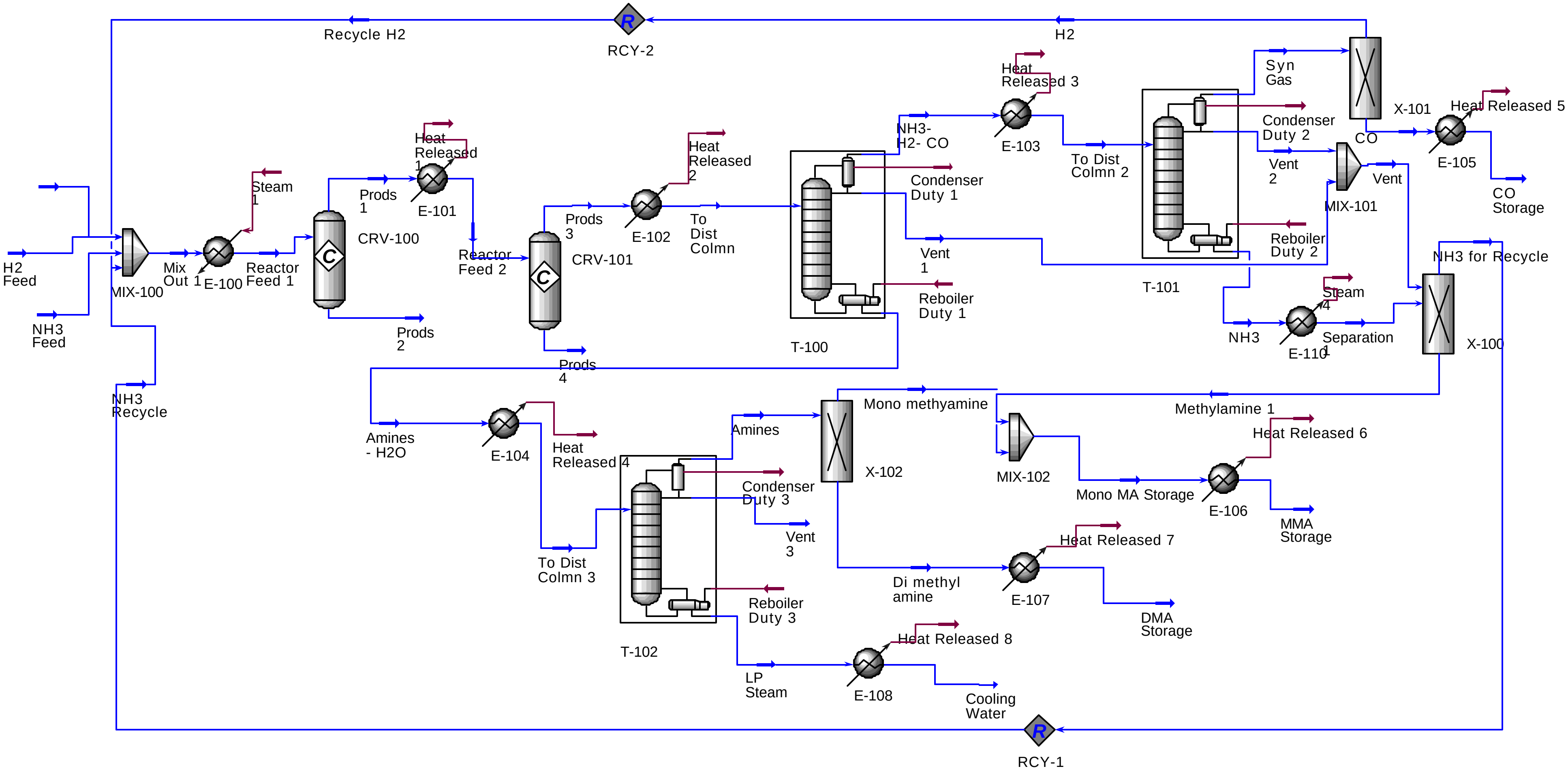


Figure 4.15. HYSYS Flow Sheet for the Production of Methylamines described by Arakawa, 1998.

A production capacity for methylamines was not available in the Louisiana Chemical & Petroleum Products List, 1998. Typical production capacities of methylamines ranged from 10,000 to 100,000 tons/year (Wells, 1999). Therefore, an average of the production capacity range specified above is used as a basis for the HYSYS simulation. Thus, a production capacity of 55,000 metric tons/year is taken as a basis. Using this production capacity as a basis, the production capacity of mono- and di-methylamines together was selected to be 55,180 metric tons per year (6,295 kg/hr).

Based on the HYSYS flow sheet, the energy required for this process was 123 x 10^6 kJ/hr. The HP steam required to provide this energy was 74 x 10^3 kg/hr, as shown in Table 4.16. The energy liberated from this process was 162 x 10^6 kJ/hr, and the cooling water required to absorb this heat was 194 x 10^4 kg/hr. Based on the HYSYS flow sheet, the amount of CO_2 that can be consumed by this process was estimated to be 104,095 metric tons per year.

Table 4.16. Economic Results for the HYSYS Simulated Methylamines Production Process described by Arakawa, 1998.

Product/Raw Material	**Flow Rate from HYSYS Simulation (kg/hr)**	**Cost/Selling Price ($/kg)**	**Source**
Carbon Dioxide	11,880	0.003	Hertwig, T. A., Private Communication, 2003
Hydrogen	1,520	0.796	Appendix B
Ammonia	2,891	0.150	Chemical Market Reporter, February 4, 2002
Mono Methylamine	3,014	1.606	Chemical Market Reporter, 2000
Di Methylamine	3,281	1.606	Chemical Market Reporter, 2000
Carbon Monoxide	781	0.031	Appendix A
High Pressure Steam	74 x 10^3	0.00865	Turton, et al., 1998
Cooling Water	194 x 10^4	6.7 x 10^{-6}	Turton, et al., 1998
Value Added Profit	$ 7,801 / hr	124 cents/kg-methylamine	

As shown in Table 4.16, the value added economic analysis gave a profit of $1.24 per kg of methylamines. This profit was based on a selling price of $1.61 per kg each of mono-and di-methylamine (Chemical Market Reporter, April 24, 2000), as shown in Table 4.16. The selling price is same for both mono- and di-methylamines (Chemical Market Reporter, April 24, 2000). The data used for the economic analysis is shown in Table 4.16. This potentially new process was included in the chemical complex.

K) Graphite Production

One potentially new process for the production of graphitic carbon (coke) was simulated using HYSYS. The results of this simulation are given below.

1) Graphite from Catalytic Fixation

The experimental study described by Nishiguchi, et al., 1998, for the production of graphitic carbon by catalytic reduction of carbon dioxide was simulated using HYSYS. A Ni supported SiO_2 catalyst was used in this study. The HYSYS flow sheet for this process is shown in Figure 4.16. The conversion of CO_2 to graphite carbon was 70% (Nishiguchi, et al., 1998). Total conversion of the reactants was achieved by the recycle. Hydrogen was obtained as a by-product. The product graphite and the by-product H_2 were pure. The reactions involved in this study are

$$2CH_4 \rightarrow 2C + 4H_2 \qquad \Delta H^o = 150 \text{ kJ/mol}, \Delta G^o = 101 \text{ kJ/mol}$$
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \Delta H^o = -165 \text{ kJ/mol}, \Delta G^o = -113 \text{ kJ/mol}$$

A production capacity for graphite was not available in the Louisiana Chemical & Petroleum Products List, 1998. Therefore, a typical production capacity of 100 million pounds per year (45,360 metric tons/year) was taken as a basis for this simulated plant. The graphite production capacity of the simulated plant was selected to be 45,960 metric tons per year (5,243 kg/hr).

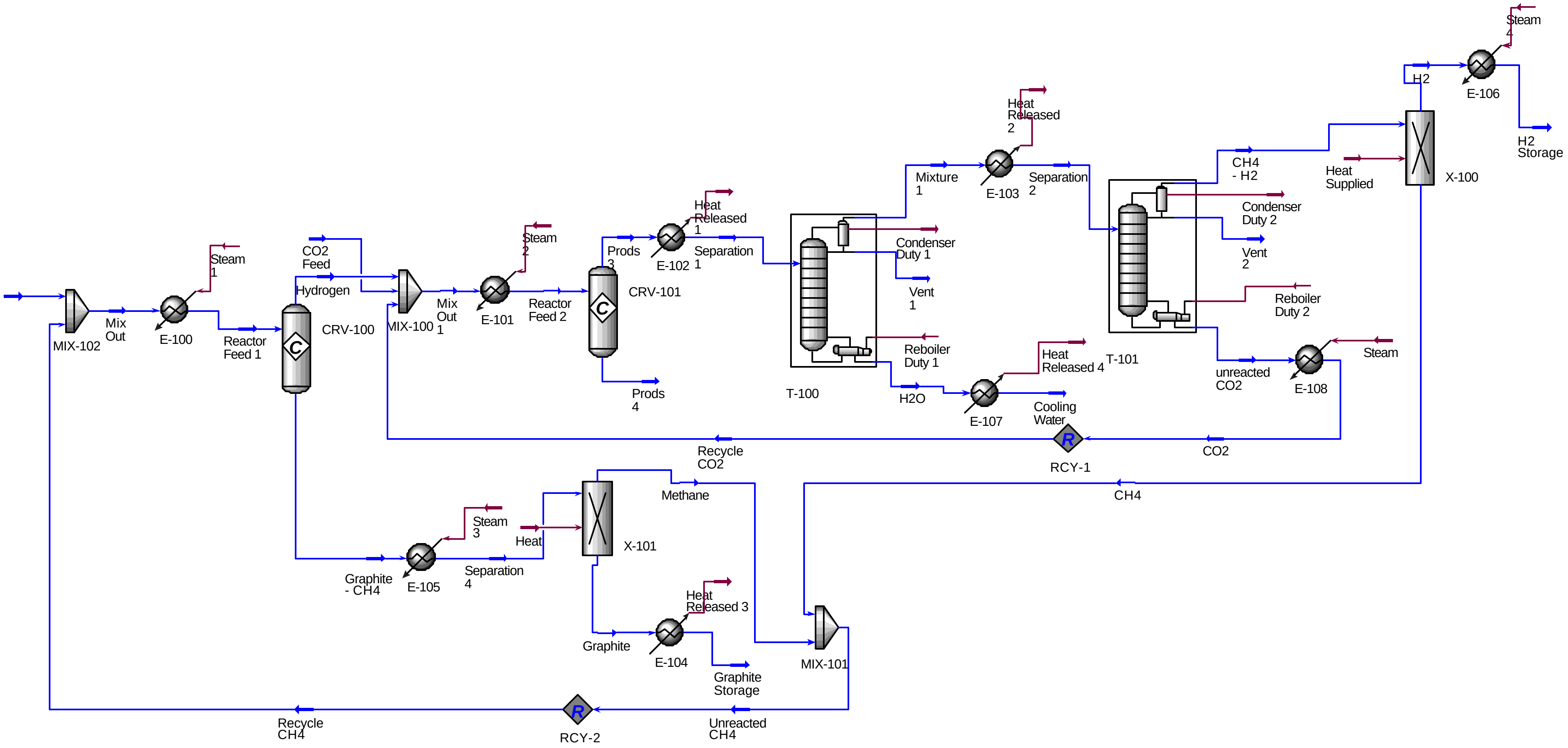


Figure 4.16. HYSYS Flow Sheet for the Production of Graphite described by Nishiguchi, et al., 1998.

Using the HYSYS flow sheet, the energy required for this process was 1,364 x 10^5 kJ/hr. The HP steam required to supply this energy was 82 x 10^3 kg/hr, as shown in Table 4.17. The energy liberated from this process was 1,313 x 10^5 kJ/hr. The cooling water required to absorb this energy was 157 x 10^4 kg/hr. Using HYSYS flow sheet, the amount of CO_2 that can be consumed by this process was estimated to be 67,540 metric tons per year.

A value added economic analysis was evaluated, and the model gave a profit of 65.6 cents per kg graphite. The economic model was based on a selling price of 88.2 cents per kg of graphite (Camford Chemical Prices, August 28, 2000), as shown in Table 4.17. The economic data for this process is given in Table 4.17. This potentially new process was included in the chemical complex.

Table 4.17. Economic Results for the HYSYS Simulated Processes for the Production of Graphite described by Nishiguchi, et al., 1998.

Product/Raw Material	**Flow Rate from HYSYS Simulation (kg/hr)**	**Cost/Selling Price ($/kg)**	**Source**
Carbon Dioxide	7,704	0.003	Hertwig, T. A., Private Communication, 2003
Methane	4,197	0.172	http://www.repartners.org/renewables/recosts.htm
High Pressure Steam	82 x 10^3	0.00865	Turton, et al., 1998
Hydrogen	349	0.796	Appendix B
Cooling Water	157 x 10^4	6.7 x 10^{-6}	Turton, et al., 1998
Graphite	5,243	0.882	Camford Chemical Prices, August 28, 2000
Value Added Profit	$ 3,437/ hr	65.6 cents/kg-graphite	

L) Production of Synthesis Gas

Four potentially new processes for the production of synthesis gas from carbon dioxide were simulated HYSYS. The reaction products CO and H_2 are separated in the processes designed using HYSYS. The results of these HYSYS simulations are given below.

1) Synthesis Gas Production by CO_2 Reforming of CH_4 over Ni/Al_2O_3 catalyst

The experimental study described by Song, et al., 2002, for the production of synthesis gas by CO_2 reforming of methane was simulated using HYSYS. A 6.6 wt% Ni/Al_2O_3 catalyst was used in this study. The conversion of CO_2 per single pass was 91.8% (Song, et al., 2002). Unreacted CO_2 and methane were recycled to achieve total conversion. Pure H_2 and CO were produced in this process. The HYSYS flow sheet of this process is shown in Figure 4.17. The following reaction occurs in the reactor.

$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \quad \Delta H^o = 247$ kJ/mol, $\Delta G^o = 171$ kJ/mol

The H_2 production capacity of this plant was selected to be 13,930 metric tons/year (15,89 kg/hr). This was based on Air Products and Chemicals INC., a hydrogen plant located in Geismar, LA, and the production capacity of this plant is 15 million cubic feet per day (13,920 metric tons/year) (Louisiana Chemical & Petroleum Products List, 1998). Along with H_2, 193,550 metric tons of CO per year (22,080 kg/hr) were produced.

Using the HYSYS flow sheet, the energy required for this process was 1,026 x 10^5 kJ/hr. The HP steam required to supply this energy was 62 x 10^3 kg/hr, as shown in Table 4.18. The energy liberated from this process was 493 x 10^4 kJ/hr, and the cooling water required to absorb this energy was 59 x 10^3 kg/hr. The amount of CO_2 that can be utilized by this potentially new process was estimated to be 152,060 metric tons per year.

The value added economic model for this process gave a profit of 17.2 cents per kg of H_2. This profit was based on a selling price of 79.6 cents per kg of H_2 (Appendix B), as shown in Table 4.18. The economic data used is listed in Table 4.18.

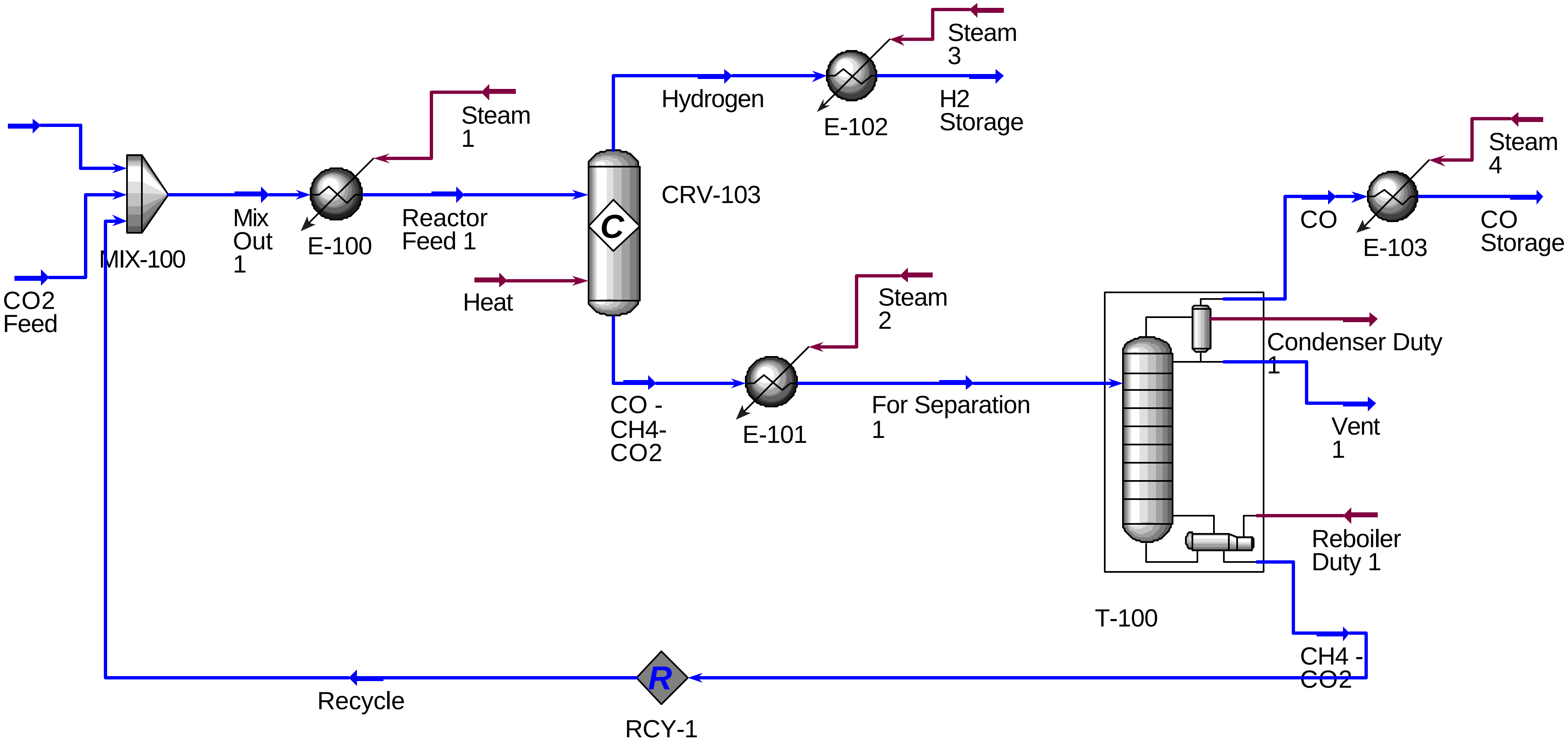


Figure 4.17. HYSYS Flow Sheet for the Co-Production of Hydrogen and CO described by Song, et al., 2002.

Table 4.18. Economic Results for the HYSYS Simulated Process for the Co-Production of CO and H_2 described by Song, et al., 2002.

Product/Raw Material	**Flow Rate from Simulation (kg/hr)**	**Cost/Selling Price ($/kg)**	**Source**
Carbon Dioxide	17,350	0.003	Hertwig, T. A., Private Communication, 2003
Methane	6,325	0.172	http://www.repartners.org/renewables/recosts.htm
Hydrogen	1,589	0.796	Appendix B
Carbon Monoxide	22,080	0.031	Appendix A
High Pressure Steam	62×10^3	0.00865	Turton, et al., 1998
Cooling Water	59×10^3	6.7×10^{-6}	Turton, et al., 1998
Value Added Profit	$ 273 / hr	17.2 cents/kg-H_2	

2) Synthesis Gas Production by CO_2 Reforming of CH_4 over Alumina catalyst

The study for the co-production of CO and H_2 by CO_2 reforming of methane described by Shamsi, 2002, was simulated using HYSYS. A noble metal catalyst of 1% rhodium supported on alumina was used. The conversion of methane for a single pass was 97% (Shamsi, 2002). Total conversion was obtained with recycle. The HYSYS flow sheet for this process is shown in Figure 4.18. The following reaction occurs in the reactor.

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \qquad \Delta H^o = 247 \text{ kJ/mol}, \Delta G^o = 171 \text{ kJ/mol}$$

The production capacity of this plant was selected to be 13,930 metric tons of H_2 per year (1,589 kg/hr). This was based on Air Products and Chemicals INC., a hydrogen plant located in Geismar, LA, and the production capacity of this plant is 15 million cubic feet per day (13,920 metric tons/year) (Louisiana Chemical & Petroleum Products List, 1998). Along with hydrogen, 193,590 metric tons of CO per year (22,084 kg/hr) were produced.

Using HYSYS flow sheet, the energy required for this process was $1{,}025 \times 10^5$ kJ/hr. The HP steam required to supply this energy was 62×10^3 kg/hr, as shown in Table

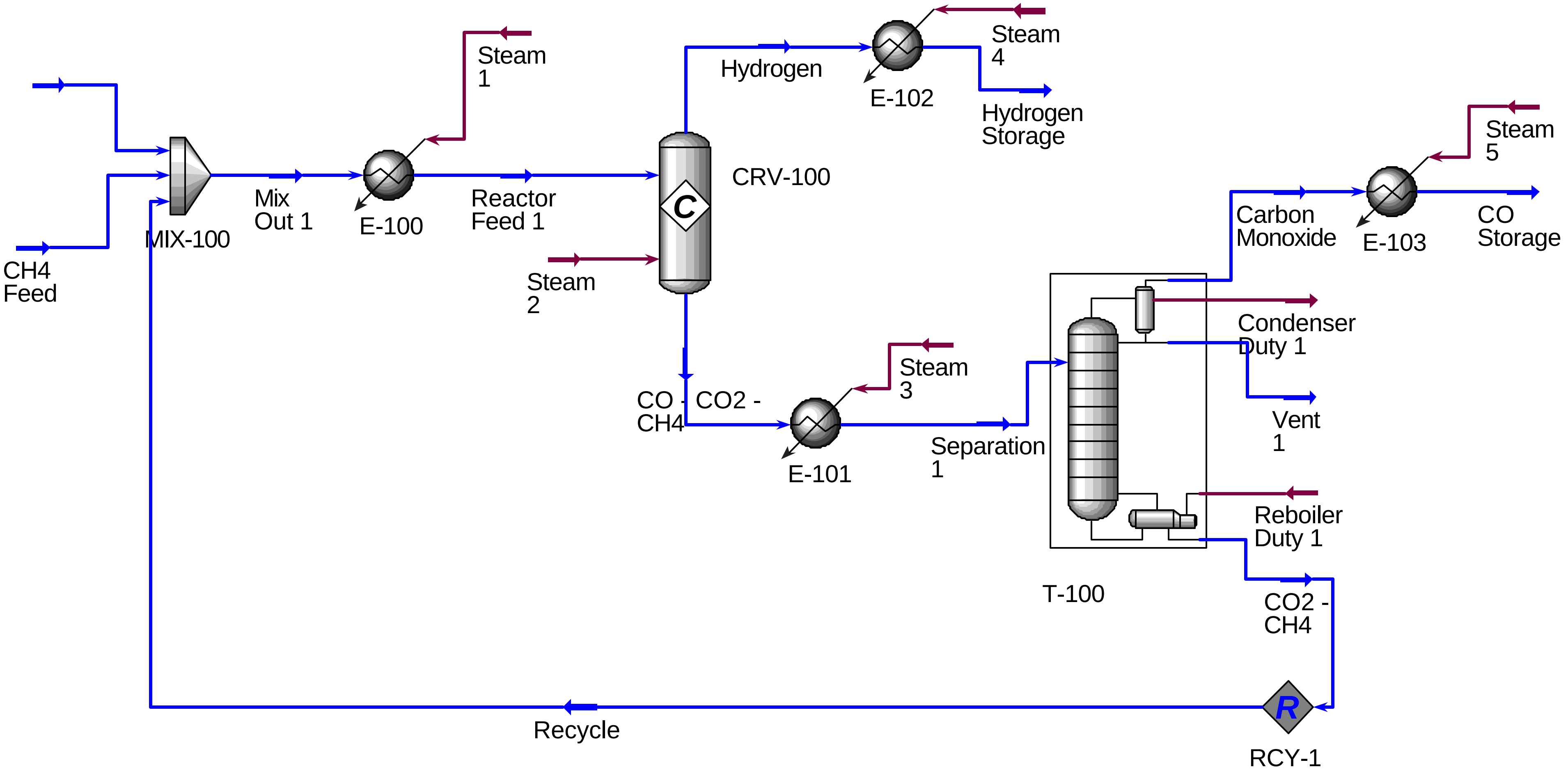


Figure 4.18. HYSYS Flow Sheet for the Co-Production of Hydrogen and CO described by Shamsi, 2002.

4.19. The energy liberated from this process was 493 x 10^4 kJ/hr, and the cooling water required to absorb this heat was 59 x 10^3 kg/hr. Based on the HYSYS flow sheet, the amount of CO_2 that can be consumed by this process was estimated to be 152,080 metric tons per year.

A value added economic analysis was evaluated, and the model gave a profit of 17.2 cents per kg H_2. This economic model was based on a selling price of 79.6 cents per kg of H_2 (Appendix B), as shown in Table 4.19. The economic data used in this process is listed in Table 4.19.

Table 4.19. Economic Results for the HYSYS Simulated Process for the Co-Production of CO and H_2 described by Shamsi, 2002.

Product/Raw Material	**Flow Rate from HYSYS Simulation (kg/hr)**	**Cost/Selling Price ($/kg)**	**Source**
Carbon Dioxide	17,350	0.003	Hertwig, T. A., Private Communication, 2003
Methane	6,324	0.172	http://www.repartners.org/renewables/recosts.htm
Hydrogen	1,589	0.796	Appendix B
Carbon Monoxide	22,084	0.031	Appendix A
High Pressure Steam	62 x 10^3	0.00865	Turton, et al., 1998
Cooling Water	59 x 10^3	6.7 x 10^{-6}	Turton, et al., 1998
Value Added Profit	$ 273 / hr	17.2 cents/kg-H_2	

3) Synthesis Gas Production over ZrO_2 catalyst

The study described by Wei, et al., 2002, for the production of CO and H_2 by CO_2 reforming over a Ni supported ultra fine ZrO_2 catalyst was simulated using HYSYS. The HYSYS flow sheet for this process is shown in Figure 4.19. The conversion of methane per pass was 86.2% (Wei, et al., 2002). Unreacted methane and CO_2 were recycled. The reaction occurring in this process is:

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \qquad \Delta H^o = 247 \text{ kJ/mol}, \Delta G^o = 171 \text{ kJ/mol}$$

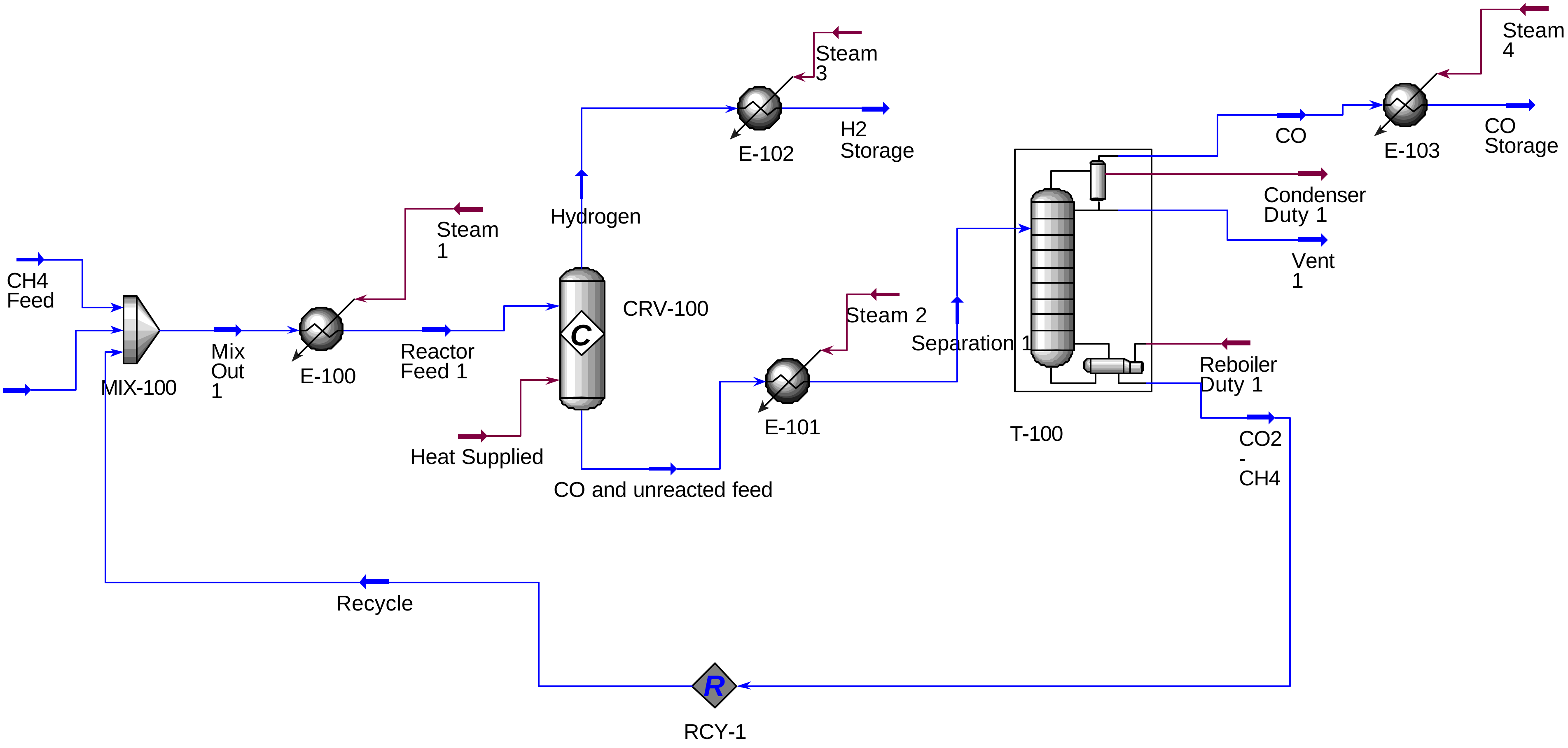


Figure 4.19. HYSYS Flow Sheet for the Co-Production of Hydrogen and CO described by Wei, et al., 2002.

The production capacity of this plant was selected to be 13,890 metric tons of H_2 per year (1,585 kg/hr). This was based on Air Products and Chemicals INC., a hydrogen plant located in Geismar, LA, and the production capacity of this plant is 15 million cubic feet per day (13,920 metric tons/year) (Louisiana Chemical & Petroleum Products List, 1998). Along with hydrogen, 193,030 metric tons of CO per year (22,020 kg/hr) were produced.

Using the HYSYS flow sheet, the energy required for this process was 1,025 x 10^5 kJ/hr. The HP steam required to supply this energy was 62 x 10^3 kg/hr, as shown in Table 4.20. The energy liberated from this process was 492 x 10^4 kJ/hr. The cooling water required to absorb this energy was 59 x 10^3 kg/hr. The amount of CO_2 that can be utilized by this process was estimated to be 151,640 metric tons per year.

The value added economic model gave a profit of 17.1 cents per kg of H_2. This profit was based on a selling price of 79.6 cents per kg of H_2 (Appendix B), as shown in Table 4.20. The economic data used is listed in Table 4.20.

Table 4.20. Economic Results for the HYSYS Simulated Process for the Co-Production of CO and H_2 described by Wei, et al., 2002.

Product/Raw Material	**Flow Rate from HYSYS Simulation (kg/hr)**	**Cost/Selling Price ($/kg)**	**Source**
Carbon Dioxide	17,300	0.003	Hertwig, T. A., Private Communication, 2003
Methane	6,307	0.172	http://www.repartners.org/renewables/recosts.htm
Hydrogen	1,585	0.796	Appendix B
Carbon Monoxide	22,020	0.031	Appendix A
High Pressure Steam	62 x 10^3	0.00865	Turton, et al., 1998
Cooling Water	59 x 10^3	6.7 x 10^{-6}	Turton, et al., 1998
Value Added Profit	$ 271 / hr	17.1 cents/kg-H_2	

4) Synthesis Gas Production over Nickel-Magnesia catalyst

The experimental study for the production of CO and H_2 by CO_2 reforming described by Tomishige, et al., 1998, was simulated using HYSYS. A nickel-magnesia solid solution catalyst was used in this study. The flow sheet of this process is shown in Figure 4.20. Unreacted methane and CO_2 were recycled, ensuring total conversion. The conversion of methane for a single pass was 80% (Tomishige, et al., 1998). The following reaction occurs in the reactor.

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \qquad \Delta H^o = 247\ \text{kJ/mol},\ \Delta G^o = 171\ \text{kJ/mol}$$

The production capacity of this plant was selected to be 13,910 metric tons of H_2 per year (1,587 kg/hr). This was based on Air Products and Chemicals INC., a hydrogen plant located in Geismar, LA, and the production capacity of this plant is 15 million cubic feet per day (13,920 metric tons/year) (Louisiana Chemical & Petroleum Products List, 1998). Along with H_2, 193,300 metric tons of CO per year (22,050 kg/hr) were produced.

Using HYSYS flow sheet, the energy required for this process was $1{,}023 \times 10^5$ kJ/hr. The HP steam required to supply this energy was 62×10^3 kg/hr, as shown in Table 4.21. The energy liberated from this process was 492×10^4 kJ/hr. The cooling water required to absorb this energy was 59×10^3 kg/hr. The amount of CO_2 that can be consumed by this potentially new process was estimated to be 151,840 metric tons per year.

A value added economic analysis was evaluated for this process, and the model gave a profit of 17.1 cents per kg H_2. This profit was based on a selling price of 79.6 cents per kg of H_2 (Appendix B), as shown in Table 4.21. The economic data used is listed in Table 4.21.

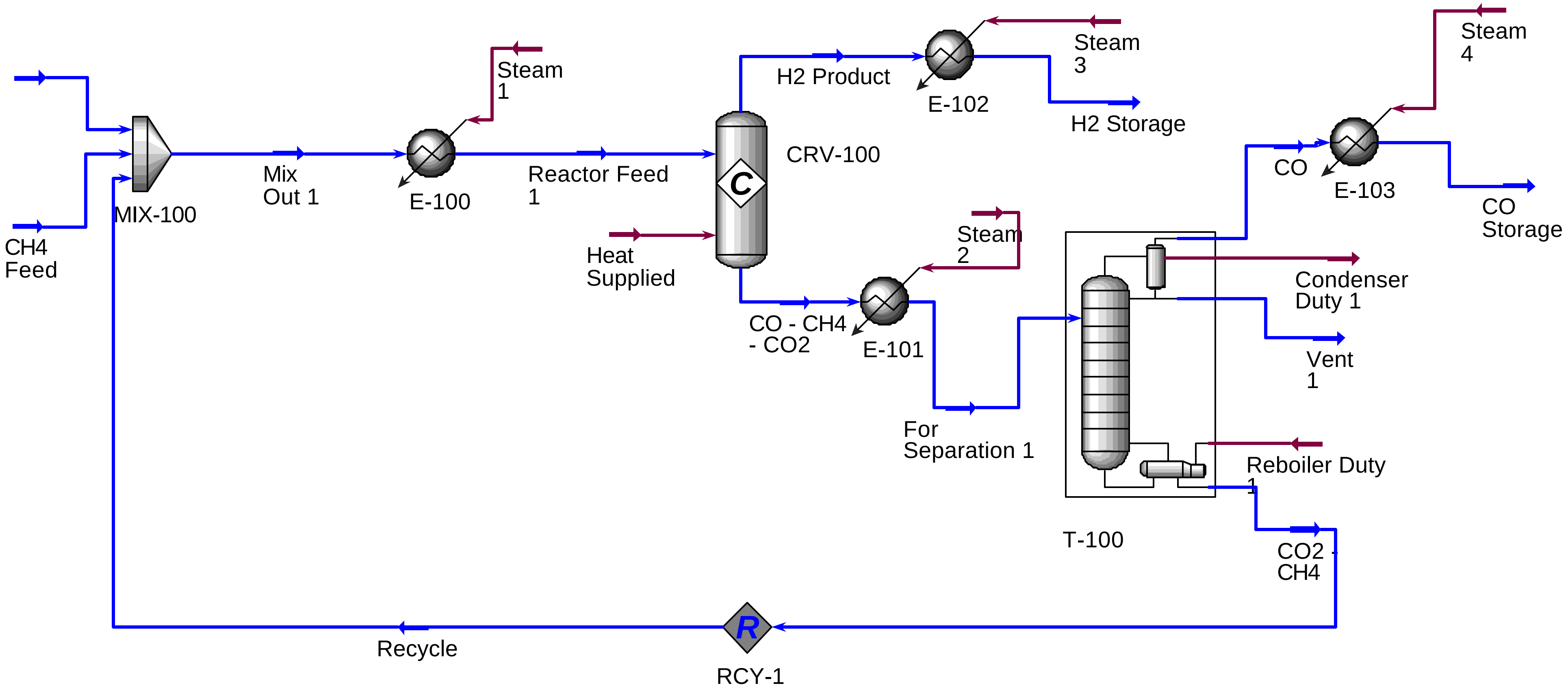


Figure 4.20. HYSYS Flow Sheet for the Co-Production of Hydrogen and CO described by Tomishige, et al., 1998.

Table 4.21. Economic Results for the HYSYS Simulated Process for the Co-Production of CO and H_2 described by Tomishige, et al., 1998.

Product/Raw Material	**Flow Rate from HYSYS Simulation (kg/h)**	**Cost/Selling Price ($/kg)**	**Source**
Carbon Dioxide	17,320	0.003	Hertwig, T. A., Private Communication, 2003
Methane	6,315	0.172	http://www.repartners.org/renewables/recosts.htm
Hydrogen	1,587	0.796	Appendix B
Carbon Monoxide	22,050	0.031	Appendix A
High Pressure Steam	62×10^3	0.00865	Turton, et al., 1998
Cooling Water	59×10^3	6.7×10^{-6}	Turton, et al., 1998
Value Added Profit	$ 272 / h	17.1 cents/kg-H_2	

5) Comparison of Synthesis Gas Plants

The four processes simulated for hydrogen and CO production were similar to each other, and only one process was selected to integrate in the chemical complex. Based on the value added economic evaluation, the experimental studies described by Shamsi, 2002, and Song, et al., 2002 gave a profit of 17.2 cents each per kg of H_2. The studies described by Wei, et al., 2002, and Tomishige, et al., 1998 gave a profit of 17.1 cents each per kg of H_2. The best process based on the value added economic profit was selected. Thus, based on valued added profit, either of the processes described by Shamsi, 2002, and Song, et al., 2002 can be integrated into the chemical complex.

The conversion of methane in the study described by Shamsi, 2002 was 97%, whereas the conversion of methane in the study described by Song, et al., 2002 was 91.8%. Thus, the study described by Shamsi, 2002 operates at a higher conversion. Based on the HYSYS flow sheets, the energy required for study described by Shamsi, 2002 was $1{,}025 \times 10^5$ kJ/hr, whereas the energy required in the study described by Song, et al., 2002 was $1{,}026 \times 10^5$ kJ/hr. Thus, the study described by Shamsi, 2002 has more advantages than the study described by Song, et al., 2002. This potentially new process was included in the chemical complex.

M) Comparison with Other, New CO_2 Processes

There has been only one announcement of a new process using CO_2 as a raw material. A 100 kg/day pilot plant is currently undergoing field tests at a power plant, and a demonstration plant is planned by Nano-Tech Research Center of the Korea Institute of Science and Technology (KIST) (Chemical Engineering, October 2003, p. 17). This process is known as camere process.

In this process, carbon dioxide and hydrogen reacts to produce CO and H_2O over a $ZnAl_2O_4$ catalyst. The reaction occurs at atmospheric pressure and 600-700˚C. Water is removed from the mixture in a dryer. In a second reactor, carbon monoxide reacts with unreacted hydrogen over a $CuO/ZnO/ZrO_2/Al_2O_3$ catalyst to produce methanol. This reaction occurs at 250-300˚C and 50-80 atm pressure. The process flow diagram for this new pilot plant is shown in Figure 4.21. The following reactions occur in this process.

$CO_2 + H_2 \rightarrow CO + H_2O$ $\Delta H^o = 41$ kJ/mol, $\Delta G^o = 29$ kJ/mol
$CO + 2H_2 \rightarrow CH_3OH$ $\Delta H^o = -90.5$ kJ/mol, $\Delta G^o = -25$ kJ/mol

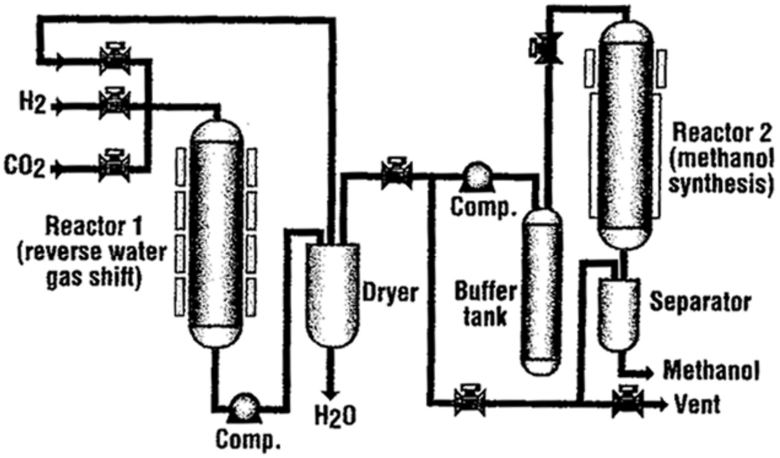


Figure 4.21. Process Flow Diagram for New Pilot Methanol Plant, from Chemical Engineering, October 2003, p. 17

The experimental study for the production of methanol described by Bonivardi, et al., 1998, follows the same reaction mechanism as that of the new process given above. This study was simulated using HYSYS, and the flow sheet was shown in Figure 4.7. The results of this simulated plant were given in Table 4.7. Thus, the new pilot plant described in Chemical Engineering, October 2003, p. 17, was compared to the HYSYS simulated plant based on the study described by Bonivardi, et al., 1998.

The new pilot plant at KIST uses $ZnAl_2O_4$ and $CuO/ZnO/ZrO_2/Al_2O_3$ catalysts, whereas the HYSYS simulated plant uses a Ca promoted Pd/SiO_2 catalyst. The first reactor in the new pilot plant operates at atmospheric pressure and 600-700˚C. The second reactor operates at 250-300˚C and 50-80 atm pressure. The reactor in the HYSYS simulated methanol plant operates at 250˚C and 3MPa (30 atm). Thus the HYSYS simulated methanol plant operates at lower temperature and pressure than the pilot plant.

The equipment required for the new pilot plant includes two reactors, dryer, buffer tank, and a separator. Based on the HYSYS simulation, the equipment required for the study described by Bonivardi, et al., 1998, include a reactor and four distillation columns.

The production cost of methanol for the new pilot plant at KIST was $ 300 per metric ton. The author reported that this process is an expensive way to make methanol. At a production cost of $ 300 per ton of methanol, the value added economic model for the HYSYS simulated methanol plant gave a profit of 5.9 cents per kg of methanol.

In summary, the HYSYS simulated methanol plant is comparable to an actual pilot plant that was started by Nano-Tech Research Center of the Korea Institute of Science and Technology (KIST). The above comparison has demonstrated that the potentially new processes developed and integrated into the chemical complex in this research have the capability of being commercialized in future.

N) Summary

The results of the HYSYS simulated plants for twenty potentially new processes were described. These processes include production of methanol, ethanol, DME, propylene, formic acid, acetic acid, styrene, methylamines, graphite, and synthesis gas. Based on the value added economic evaluation, fourteen potentially new processes were included in the chemical complex. The processes included in the chemical complex along with the value added profit are given in Table 4.22. The processes that were not included in the chemical complex are listed in Table 4.23.

Table 4.22. Potentially New Processes Integrated into the Chemical Complex

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

Table 4.23. New Processes Not Included into the Chemical Complex

Product	**Synthesis Route**	**Value Added Profit (cents/kg)**	**Reference**
Methanol	CO_2 hydrogenation	-7.6	Toyir, et al., 1998
Ethanol	CO_2 hydrogenation	31.6	Inui, 2002
Styrene	Ethylbenzene dehydrogenation	4.5	Sakurai, et al., 2000
Hydrogen/Synthesis Gas	Methane reforming	17.2	Song, et al., 2002
Hydrogen/Synthesis Gas	Methane reforming	17.1	Wei, et al., 2002
Hydrogen/Synthesis Gas	Methane reforming	17.1	Tomishige, et al., 1998

A 100 kg/day pilot plant for methanol production is currently undergoing field tests at a power plant, and a demonstration plant is planned by Nano-Tech Research Center of the Korea Institute of Science and Technology (KIST) (Chemical Engineering, October 2003, p. 17). This pilot plant was compared to the results of the HYSYS simulated methanol plant based on the study described by Bonivardi, et al., 1998. The comparison of results has demonstrated that the potentially new processes integrated into the chemical complex have the capability of being commercialized in future.

The selected fourteen potentially new processes will be integrated into the chemical production complex in the lower Mississippi River Corridor using Chemical Complex and Cogeneration Analysis System. The results of the integration of these processes will be discussed in the next chapter.

CHAPTER FIVE: RESULTS FROM INTEGRATING NEW PROCESSES IN THE CHEMICAL COMPLEX

The results of the HYSYS simulations of twenty potentially new processes were given in Chapter Four. Based on the value added economic analysis, fourteen potentially new processes were selected and integrated into the chemical production complex in lower Mississippi River Corridor. These potentially new plants were evaluated using Chemical Complex and Cogeneration Analysis System. These results are analyzed in this chapter.

The Chemical Complex and Cogeneration Analysis System determines the best configuration of plants in a chemical complex based on the AIChE Total Cost Assessment (TCA) for economic, energy, environmental and sustainable costs. It also incorporates EPA Pollution Index Methodology (WAR) algorithm. A more detailed description of the System was given in Chapter Two.

A) Application of Chemical Complex and Cogeneration Analysis System

The Chemical Complex and Cogeneration Analysis system has been applied to an agricultural chemical production complex in the lower Mississippi River Corridor (Hertwig, et al., 2002). The diagram of plants in the agricultural chemical complex is shown in Figure 5.1, and is called the base case of existing plants. There are thirteen production units plus associated utilities for power, steam and cooling water and facilities for waste treatment. A production unit contains more than one plant. For example, the sulfuric acid production unit contains five plants owned by two companies (Hertwig, et al., 2002). Here, ammonium plants produce 0.75 million tons/year of carbon dioxide, and methanol, urea, and acetic acid plants consume 0.14 million tons of carbon dioxide. This leaves a surplus of 0.61 million tons/year of high quality carbon dioxide, as shown in

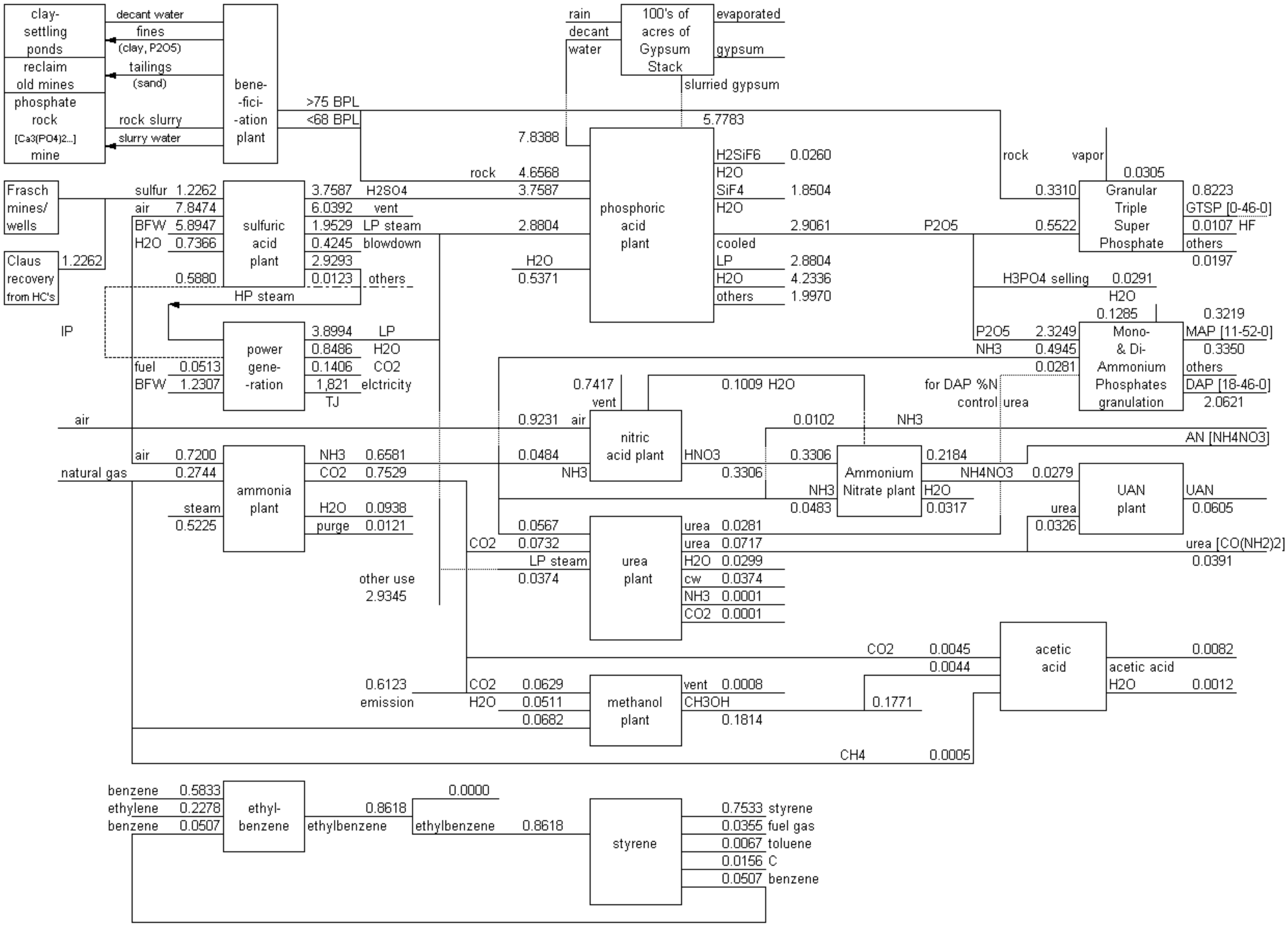


Figure 5.1. Chemical Production Complex Based on Plants in Lower Mississippi River Corridor, Base Case. Flow Rates Million TPY

Figure 5.1. This high purity carbon dioxide can be used in other processes rather than being vented to the atmosphere. A table showing the flow rates of all streams among the plants in the base case is given in Appendix D.

For this base case, there were 362 equality constraints that describe material and energy balances, rate equations and equilibrium relations for the plants. Also, there were 28 inequality constraints equations that describe the product demand, availability of raw materials, and range on the capacities of individual plants in the chemical complex (Hetrwig, et al., 2002). The model of the complex is available in the Chemical Complex Analysis program and users manual available from the LSU Mineral Processing Research Institute's website, http://www.mpri.lsu.edu (Xu, et al., 2003). Also, the model is available in the CD included with this thesis.

As shown in Figure 5.1, the raw materials used in the chemical complex include air, water, natural gas, sulfur, ethylene, benzene and phosphate rock. The products include mono- and di- ammonium phosphates (MAP and DAP), granular triple super phosphate (GTSP), urea ammonium nitrate solution (UAN), ammonium sulfate, phosphoric acid, acetic acid, urea, styrene and methanol. Intermediates formed include urea, nitric acid, sulfuric acid, ammonia, methanol, CO_2, ethylbenzene and phosphoric acid. The intermediate nitric acid is used to produce ammonium nitrate; ammonia to produce urea, nitric acid; urea to produce UAN and mono-di- ammonium phosphates (MAP and DAP) and GTSP; methanol to produce acetic acid; and sulfuric acid to produce phosphoric acid and ammonium nitrate. Carbon dioxide is used to produce methanol and acetic acid in the chemical complex. Benzene and ethylene are used to produce ethylbenzene. This intermediate ethylbenzene is used to produce styrene.

The chemical production complex shown in Figure 5.1 was expanded into a superstructure by integrating the fourteen potentially new processes that were selected based on the evaluations of HYSYS simulations. These fourteen potentially new processes were listed in Chapter Four in Table 4.22. These new processes were selected based on the value added economic profit, which was obtained based on the information from HYSYS simulations. The results of these simulations were given in Chapter Four. These fourteen potentially new 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 synthesis gas.

Four other new processes developed by Xu, et al., 2003, that do not use CO_2 as a raw material were included in the superstructure. These include two processes for phosphoric acid production and two processes for recovering sulfur and sulfur dioxide. There were two alternative plants added to produce phosphoric acid. One was the electric furnace process, which has high energy costs but produces calcium oxide. In the other process, calcium phosphate ore reacts with HCl to produce phosphoric acid. Two gypsum used as a feedstock plants, were included to reuse the gypsum waste. One would reduce gypsum to sulfur dioxide that was recycled to sulfuric acid plant. The other would reduce gypsum to sulfur and sulfur dioxide, which were also recycled to sulfuric acid plant. Thus, a total of eighteen processes were included in the superstructure.

The diagram of plants in the superstructure is shown in Figure 5.2. A convenient way to show the plants in base case and the plants added to form the superstructure is given in Table 5.1. This expanded complex gives alternative ways to produce intermediates that reduce wastes and energy and consume greenhouse gases.

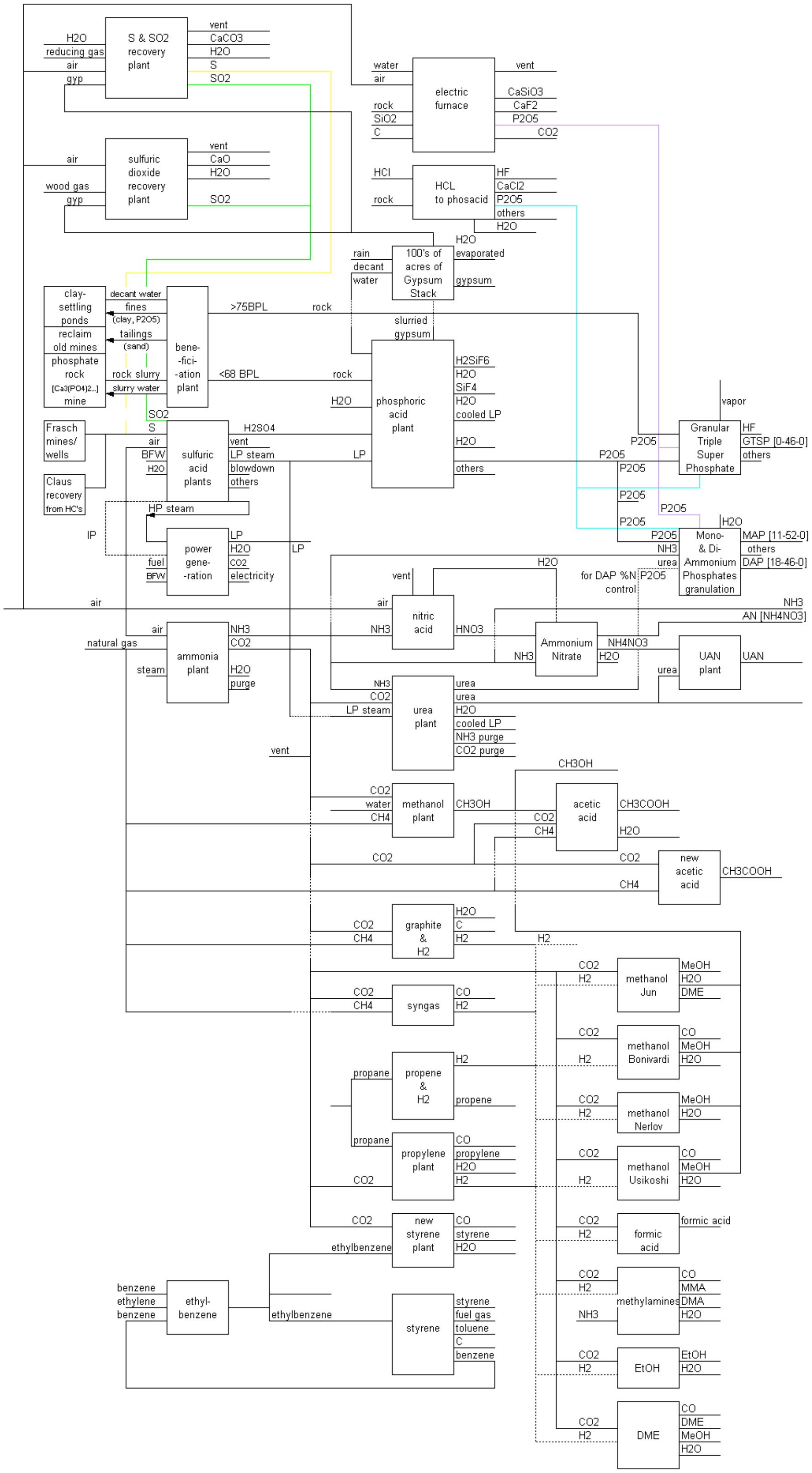


Figure 5.2. Chemical Production Complex Based on Plants in the Lower Mississippi River Corridor, Superstructure.

Table 5.1. Processes in Chemical Production Complex Base Case and Superstructure

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 & DAP Power generation Contact process for Sulfuric acid Wet process for phosphoric acid Acetic acid - standard method Ethylbenzene Styrene	Electric furnace process for phosphoric acid HCl process for phosphoric acid SO_2 recovery from gypsum process S & SO_2 recovery from gypsum process Methanol - Bonivardi, et al., 1998 Methanol – Jun, et al., 1998 Methanol – Ushikoshi, et al., 1998 Methanol – Nerlov and Chorkendorff, 1999 Ethanol DME Formic Acid Acetic acid - new method Styrene - new method Methylamines Graphite Hydrogen/Synthesis Gas Propylene from CO_2 Propylene from propane dehydrogenation

In summary, the superstructure included three options for producing phosphoric acid, five options for producing methanol, two options each for producing acetic acid, styrene and propylene. It also included two options for recovering sulfur and sulfur dioxide. It included one option each for producing sulfuric acid, nitric acid, urea, UAN, GTSP, MAP & DAP, ethylbenzene, graphite, synthesis gas, DME, formic acid, ethanol, and methylamines.

The superstructure has 830 continuous variables, 23 integer variables, 750 equality constraint equations for material and energy balances and 64 inequality constraints for availability of raw materials, demand for product and capacities of the plants in the complex.

For the base case and superstructure, a value added economic model was expanded to account for environmental and sustainable costs. Value added economic model is the difference between sales and the cost of raw materials and utilities. The sales prices for products and the costs of raw materials are given in Table 5.2.

Based on the data provided by Amoco, Dupont and Novartis in the AIChE/CWRT report, environmental costs were estimated to be 67% of the raw material costs (Constable, et al., 1999). 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/CWRT report where CO_2 emissions had a sustainable cost of \$3.25 per ton of CO_2. As shown in Table 5.2, a cost of \$3.25 was charged as a cost to plants that emit CO_2, and a credit of twice this cost (\$6.50) was given to plants that utilize CO_2. This credit was included for steam produced from waste heat by the sulfuric acid plant displacing steam produced from a package boiler firing hydrocarbons and emitting CO_2.

The System was used to obtain the optimum configuration of plants from the superstructure. Thus, the System determined the best processes to be integrated into the chemical complex. The new processes were selected by the System based on the following constraints.

For methanol, styrene and acetic acid, the commercial processes and the corresponding potentially new processes were compared to each other, and the best processes were selected. For the other potentially new process, there were no commercial plants in the base case to compare. Thus, the System selects the optimal configuration of these new plants based on economic, environmental and sustainable costs.

The constraint on production capacity of a process is as follows. The production capacities of the potentially new processes were given in Chapter Four while describing

Table 5.2. Raw Material Costs, Product Prices and Sustainable Costs
Source: Green Market Sheet, Constable, et al., 1999, Chemical Market Reporter, Camford Chemical Prices, C & EN, June 2003, p.15 and Internet

Raw Materials	Cost ($/mt)	Sustainable Costs and Credits	Cost ($/mt)	Products	Price ($/mt)
Natural gas	172	Credit for CO_2 consumption	6.50	Ammonia	150
				Methanol	300
Phosphate rock		Debit for CO_2 production	3.25	Acetic acid	1,034
Wet process	27	Credit for HP steam	10	GTSP	142
Electrofurnace	24	Credit for IP steam	6.40	MAP	180
HCl process	25	Credit for gypsum consumption	5	DAP	165
GTSP process	30	Debit for gypsum production	2.5	NH_4NO_3	153
HCl	50	Debit for NO_x production	1,025	Ethanol	670
Sulfur		Debit for SO_2 production	150	Ethylbenzene	551
Frasch	42			Propylene	240
Claus	38			CO	31
C electrofurnace	760			Graphite	882
Ethylene	446			Hydrogen	796
Benzene	257			Styrene	705
Propane	163			Toluene	238
Market cost for short term purchase				Fuel gas	596
				Formic acid	690
Reducing gas	1,394			MMA	1,606
Wood gas	634			DMA	1,606
				DME	946

the results for HYSYS simulations, and these values were taken as upper bounds. These production capacities were based on actual plants, and it would be realistic if the processes selected in the optimal structure operate at capacities close to their corresponding upper bounds. Since the problem was solved using a Mixed Integer Non-Linear Programming (MINLP) approach, the selected processes would operate with a capacity in the range specified by their upper and lower bounds. In this point of view, the lower bound of the production capacity should be close to the upper bound to the extent possible. However, if the lower bound is too close to the upper bound, then the System would have limited options for selecting the optimum configuration of plants. Consequently, the lower bound should differ significantly from the upper bound. Thus, the lower bound for the production capacity was selected as half the value of upper bound. Thus, if a process is selected, it has to operate at least at the lower bound of its production capacity, which is half of the upper bound. A table showing the upper bounds and lower bounds of the production capacities of all the plants in the chemical complex is shown in Table 5.3.

For each plant, binary variables are associated with their production capacities. If the binary variable of a process is zero, then the production capacity of that process is zero. Thus, the processes for which the binary variables are zero are not operated in the optimal structure. If the binary variable of a process is one, then the plant operates at least at its lower bound on the production capacity. Such a plant operates at a production capacity in the range specified by their upper and lower bounds as the problem was solved using MINLP approach. Thus, the processes for which the binary variables are one are operated in the optimal structure.

Table 5.3. Upper and Lower Bounds of Production Capacities of Plants in the Chemical Complex

Plant Name	**Upper Bound of Capacity (metric tons/year)**	**Lower Bound of Capacity (metric tons/year)**
Ammonia	658,061	329,030
Nitric acid	178,547	89,273
Ammonium Nitrate	226,796	113,398
Urea	99,790	49,895
Methanol	181,437	90,718
UAN	60,480	30,240
MAP	321,920	160,960
DAP	2,062,100	1,031,050
GTSP	822,300	411,150
Contact process sulfuric acid	3,702,372	1,851,186
Wet process phosphoric acid	1,394,978	697,489
Ethylbenzene	861,826	430,913
Styrene	771,108	385,554
Acetic acid	8,165	4,082
Electric furnace phosphoric acid	1,394,978	697,489
HCl to phosphoric acid	1,394,978	697,489
New acetic acid	8,165	4,082
SO_2 recovery from gypsum	1,804,417	902,208
Sulfur & SO_2 recovery from gypsum	903,053	451,526
Graphite	45,961	22,980
Hydrogen/Synthesis gas	13,933	6,966
Propene & H_2	41,791	20,896
Propene using CO_2	41,429	20,714
New styrene	362,237	181,118
New methanol – Ushikoshi	479,780	239,890
New methanol – Nerlov	480,000	240,000
New methanol – Jun	479,526	239,763
New methanol – Bonivardi	477,449	238,724
Formic acid	77,948	38,974
Methylamines	26,397	13,198
Ethanol	103,728	51,864
DME	45,454	22,727

Three different case studies were evaluated to demonstrate the capability of the System. In the first case study, the System would select the optimum configuration of plants based on economic, environmental and sustainable costs. In the second case study, the System would determine the optimum configuration of plants for consuming all of the CO_2 from the ammonia plant. In the third case study, the System would select the optimum configuration of plants for consuming all of the CO_2 from ammonia plant operating at full capacity. The results of these three different case studies are analyzed now.

B) Case Study One - Optimal Configuration of Plants

The optimal structure from the superstructure is shown in Figure 5.3, and a convenient way to show the new plants selected in the optimal structure is shown in Table 5.4. The new acetic acid process replaced the commercial acetic acid plant in the chemical complex. Thus, the System determined that this potentially new process was more profitable than the existing plant in the base case. The new styrene process and the new methanol processes were not selected in the optimal structure. Thus, the System determined that their corresponding commercial processes present in the base case were more profitable. The commercial process for methanol does not use expensive hydrogen as a raw material, but the new methanol processes use hydrogen as a raw material. The new processes for formic acid, methylamines, graphite and synthesis gas were selected by the System. The processes for propylene, DME and ethanol were not selected in the optimal structure. A table showing the flow rates of all streams among the plants in the optimal structure for the case study one is given in Appendix D.

In summary, out of the eighteen processes integrated in the superstructure, the System selected five potentially new processes in the optimal structure. These include acetic acid, graphite, formic acid, methylamines, and synthesis gas production. The plants present in the optimal structure are shown in Table 5.4. Also, the plants that were not

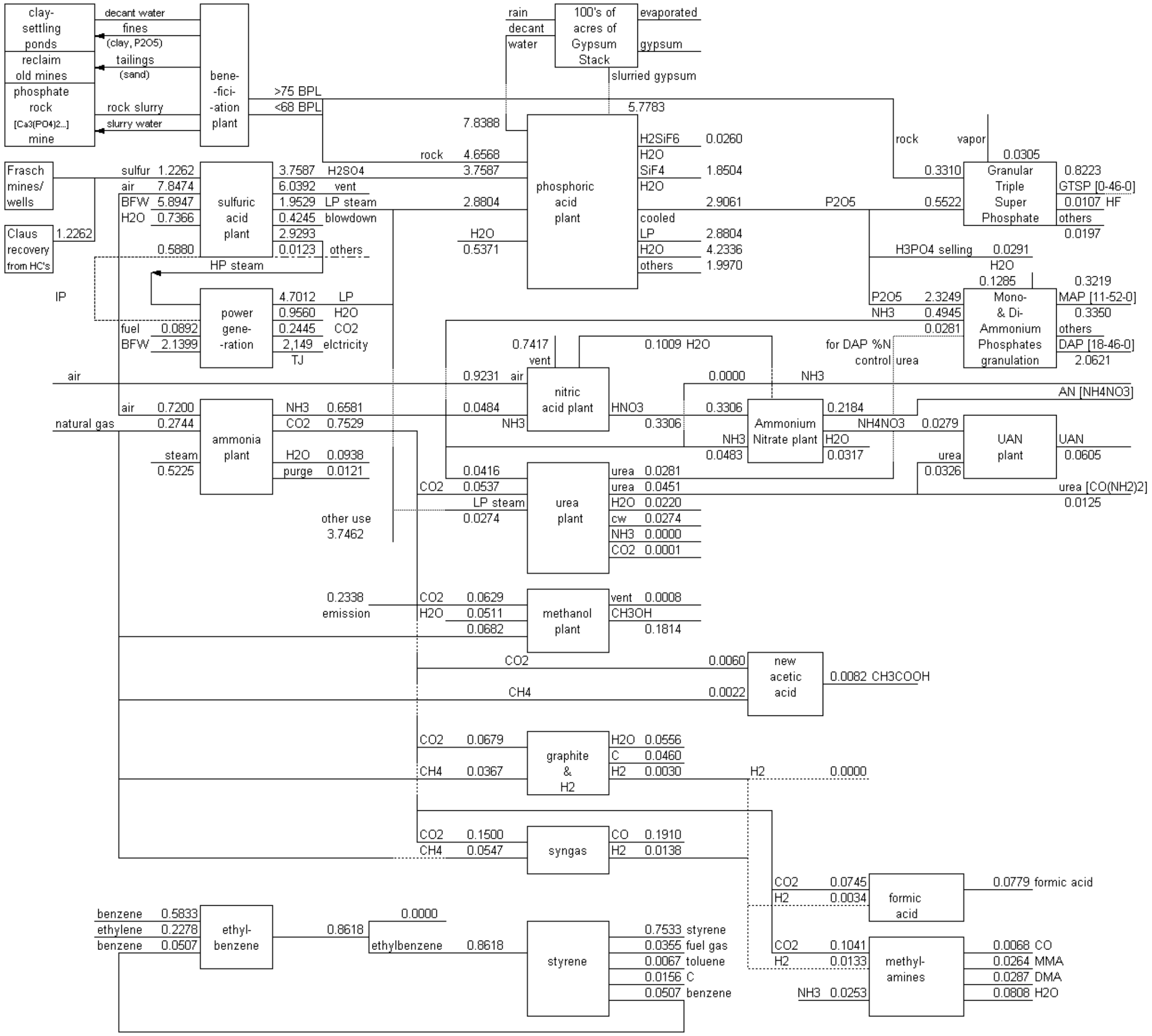


Figure 5.3. Chemical Production Complex Based on Plants in Lower Mississippi River Corridor, Optimal Structure from Superstructure, Case Study One. Flow Rates Million TPY

selected in the optimal structure are shown in this table. As shown in Table 5.4, all the plants in the base case except for the standard acetic acid plant were selected in the optimal structure.

Table 5.4. Plants in the Optimal Structure from superstructure, Case Study One.

Plants in the Base Case	**New Plants in the Optimal Structure**
Ammonia Nitric acid Ammonium nitrate Urea UAN Methanol Granular triple super phosphate (GTSP) MAP & DAP Power generation Contact process for Sulfuric acid Wet process for phosphoric acid Ethylbenzene Styrene	Formic acid Acetic acid – new method Methylamines Graphite Hydrogen/Synthesis gas
Plants Not in the Base Case	**New Plants Not in the Optimal Structure**
Acetic acid - standard method	Electric furnace process for phosphoric acid HCl process for phosphoric acid SO_2 recovery from gypsum process S & SO_2 recovery from gypsum process Methanol - Bonivardi, et al., 1998 Methanol – Jun, et al., 1998 Methanol – Ushikoshi, et al., 1998 Methanol – Nerlov and Chorkendorff, 1999 Ethanol DME Styrene - new method Propylene from CO_2 Propylene from propane dehydrogenation

From the results, it was observed that the potentially new processes present in the optimal structure were operated at full production capacities. Also, the ammonia plant was operated at full production capacity. A comparison of the results of the optimal structure with the results of the base case for the chemical production complex is shown in Table 5.5.

All of the five new processes present in the optimal structure use CO_2 as a raw material. Therefore, the consumption of CO_2 increased, and CO_2 vented from the ammonia plant decreased in the complex. For the base case, 0.75 million tons of CO_2 per year were available from ammonia plant, and 0.14 million tons per year were consumed in the methanol, urea and acetic acid plants. Thus, 0.61 million tons of CO_2 per year were vented from the ammonia plant. In the optimal solution, 0.75 million tons of CO_2 per year were available from ammonia plant, and 0.52 million tons per year were consumed in methanol, urea, acetic acid, graphite, synthesis gas, formic acid and methylamines plants. Thus, 0.23 million tons of CO_2 per year were vented from the ammonia plant. The utilization of CO_2 increased from 0.14 million tons per year to 0.52 million tons per year**,** and the CO_2 vented from the ammonia plant decreased from 0.61 to 0.23 million tons per year in the chemical production complex.

Table 5.5. Comparison of results for the Optimal Structure from Superstructure and Base Case, Case Study One.

		Base case		**Optimal structure**	
Profit (U.S.$/year)		378,325,617		528,839,047	
Environmental cost (U.S.$/year)		334,403,783		349,412,803	
Sustainability cost (U.S.$/year)		-18,039,196		-21,405,665	
Plant name	**Capacity (t/year) (upper-lower bounds)**	**Capacity (t/year)**	**Energy Requirement (TJ/year)**	**Capacity (t/year)**	**Energy Requirement (TJ/year)**
Ammonia	329,030-658,061	658,061	3,820	658,061	3,820
Nitric acid	89,273-178,547	178,525	-648	178,525	-648
Ammonium nitrate	113,398-226,796	226,796	117	226,796	117
Urea	49,895-99,790	99,790	128	73,188	94
Methanol	90,718-181,437	181,437	2,165	181,437	2,165
UAN	30,240-60,480	60,480	0	60,480	0
MAP	160,960-321,920	321,912		321,912	
DAP	1,031,050-2,062,100	2,062,100	2,137	2,062,100	2,137
GTSP	411,150-822,300	822,284	1,036	822,284	1,036
Contact process sulfuric acid	1,851,186-3,702,372	3,702,297	-14,963	3,702,297	-14,963
Wet process phosphoric acid	697,489-1,394,978	1,394,950	7,404	1,394,950	7,404
Ethylbenzene	430,913-861,826	861,827	-755	861,827	-755
Styrene	385,554-771,108	753,279	3,318	753,279	3,318
Acetic acid	4,083-8,165	8,165	268	0	0
Electric furnace phosphoric acid	697,489-1,394,978	na	na	0	0

Table 5.5. (Continued).

HCl to phosphoric acid	697,489-1,394,978	na	na	0	0
New Acetic acid	4,083-8,165	na	na	8,165	8
SO_2 recovery from gypsum	902,208-1,804,417	na	na	0	0
S & SO_2 recovery from gypsum	451,527-903,053	na	na	0	0
Graphite & H_2 from CO_2 & CH_4	22,980-45,961	na	na	45,961	1,046
Syngas	6,966-13,933	na	na	13,773	884
Propene & H_2	20,896-41,791	na	na	0	0
Propene using CO_2	20,714-41,429	na	na	0	0
New Styrene	181,118-362,237	na	na	0	0
New methanol-Ushikoshi	239,890-479780	na	na	0	0
New methanol-Nerlov	240,000-480,000	na	na	0	0
New methanol-Jun	239,763-479,526	na	na	0	0
New methanol-Bonivardi	238,724-477,449	na	na	0	0
Formic acid	38,974-77,948	na	na	77,948	14
Methylaimines	13,198-26,397	na	na	26,397	1,109
Ethanol	51,864-103,728	na	na	0	0
Dimethylether	22,727-45,454	na	na	0	0
Ammonia sale		10,227		0	
Ammnium Nitrate sale		218,441		218,441	
Urea sale		39,076		12,474	
Wet process phosphoric acid sale		13,950		13,950	
Ethylbenzene sale		0		0	
CO_2 vented		612,300		233,800	
Total energy requirement			4,028		6,786

The important results from Figure 5.3 and Table 5.5 are shown in Table 5.6. From the results in Table 5.6, the following observations were made. For optimal solution, the profit increased about 40% from the base case to the optimal solution. The environmental costs increased about 4.5%, and the sustainable costs decreased by 17%.

Table 5.6. Results for the Optimal Structure from Superstructure and Base Case, Case Study One.

Property	**Base Case**	**Optimal Structure**
Profit	\$ 378 million/year	\$ 529 million/year
Environmental Cost	\$ 334 million/year	\$ 349 million/year
Sustainable Cost	\$ -18 million/year	\$ -21 million/year
CO_2 Utilized from NH_3 Plant	0.14 million tons/year	0.52 million tons/year
CO_2 Available from NH_3 Plant	0.61 million tons/year	0.23 million tons/year

C) Case Study Two – Consuming All of the CO_2 from Ammonia Plant

The System determined the optimum configuration of plants for consuming all of the CO_2 from the ammonia plant. The optimal structure from the superstructure is shown in Figure 5.4, and a convenient way to show the new plants selected in the optimal structure is shown in Table 5.7. A table showing the flow rates of all streams among the plants in the optimal structure for the case study two is given in Appendix D.

Table 5.7. Plants in the Optimal Structure from Superstructure, Case Study Two.

Plants in the Base Case	**New Plants in the Optimal Structure**
Ammonia Nitric acid Ammonium nitrate Urea UAN Methanol Granular triple super phosphate (GTSP) MAP & DAP Power generation Contact process for Sulfuric acid Wet process for phosphoric acid Ethylbenzene Styrene	Formic acid Acetic acid – new method Methylamines Graphite Hydrogen/Synthesis gas Propylene from CO_2
Plants Not in the Base Case Acetic acid - standard method	**New Plants Not in the Optimal Structure** Electric furnace process for phosphoric acid HCl process for phosphoric acid SO_2 recovery from gypsum process S & SO_2 recovery from gypsum process Methanol - Bonivardi, et al., 1998 Methanol – Jun, et al., 1998 Methanol – Ushikoshi, et al., 1998 Methanol – Nerlov and Chorkendorff, 1999 Ethanol DME Styrene - new method Propylene from propane dehydrogenation

The System selected six new processes out of the eighteen processes integrated in the superstructure. The new acetic acid plant replaced the commercial plant present in the base case. The new styrene plant and the new methanol plants were not selected in the optimal structure. The new processes for formic acid, methylamines, graphite and synthesis gas were selected by the System. Also, the new process for propylene

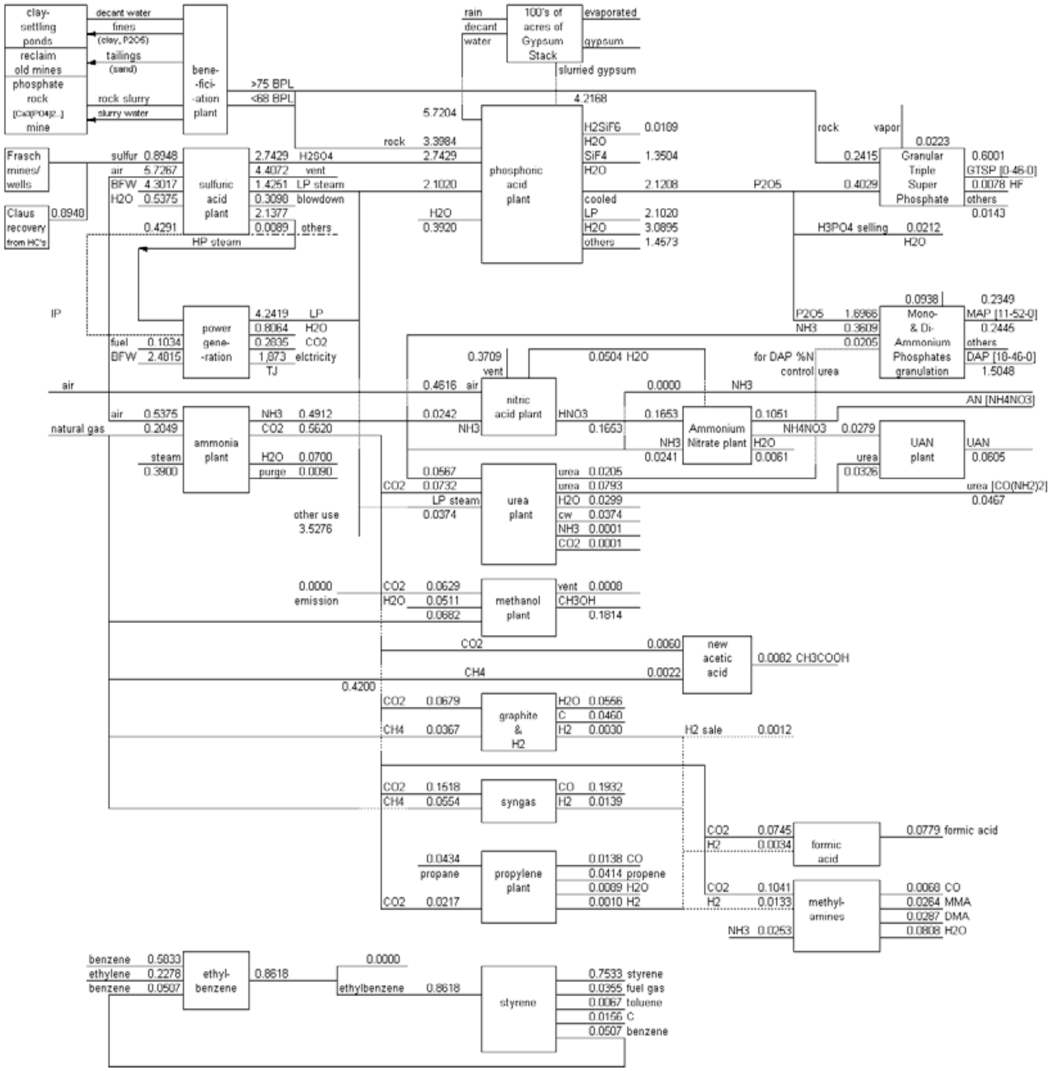


Figure 5.4. Chemical Production Complex Based on Plants in Lower Mississippi River Corridor, Optimal Structure from Superstructure, Case Study Two. Flow Rates Million TPY

production that uses CO_2 as a raw material was selected. The new processes DME and ethanol were not selected in the optimal structure. All the plants in the base case except for the standard acetic acid plant were selected in the optimal structure.

From the results, it was observed that the six potentially new processes present in the optimal structure were operated at full production capacities. All of the six new processes in the optimal structure use CO_2 as a raw material. In this case, it was observed that the ammonia plant was not operated at full production capacity as in the case of study one. The ammonia plant was operated at 491,000 metric tons/year in study two, whereas it was operated at full capacity (658,000 metric tons/year) in study one.

A comparison of the results of the optimal structure with the results of the base case for the chemical production complex was made. These results were listed in Table 5.8. In this case, all of the carbon dioxide available from the ammonia plant was consumed, but the profit decreased from \$529 millions per year in case study one to \$469 millions per year in case study two. This decline in profit was expected as the new propylene process was selected in the optimal structure. The new propylene process was not profitable after incorporating environmental and sustainable costs in the economic model. However, to consume all of the carbon dioxide available from the ammonia plant, this new process was selected by the System along with other new processes.

For the base case, 0.75 million tons of carbon dioxide per year were available from ammonia plant, and 0.14 million tons per year were consumed in the methanol, urea and acetic acid plants. Thus, 0.61 million tons of carbon dioxide per year were vented from the ammonia plant. In the optimal solution, 0.56 million tons of carbon dioxide per year were available from ammonia plant, and all of the carbon dioxide was consumed in methanol, urea, acetic acid, graphite, synthesis gas, formic acid, propylene and methylamines plants.

Table 5.8. Comparison of results for the Optimal Structure from Superstructure and Base Case, Case Study Two.

		Base case		**Optimal structure**	
Profit (U.S.$/year)		378,325,617		469,358,203	
Environmental cost (U.S.$/year)		334,403,783		315,020,497	
Sustainability cost (U.S.$/year)		-18,039,196		-17,037,558	
Plant name	**Capacity (t/year) (upper-lower bounds)**	**Capacity (t/year)**	**Energy Requirement (TJ/year)**	**Capacity (t/year)**	**Energy Requirement (TJ/year)**
Ammonia	329,030-658,061	658,061	3,820	491,214	2,852
Nitric acid	89,274-178,547	178,525	-648	89,274	-324
Ammonium nitrate	113,398-226,796	226,796	117	113,412	27
Urea	49,895-99,790	99,790	128	99,790	128
Methanol	90,718-181,437	181,437	2,165	181,437	2,165
UAN	30,240-60,480	60,480	0	60,480	0
MAP	160,960-321,920	321,912		234,917	
DAP	1,031,050-2,062,100	2,062,100	2,137	1,504,832	1,560
GTSP	411,150-822,300	822,284	1,036	600,067	756
Contact process sulfuric acid	1,851,186-3,702,372	3,702,297	-14,963	2,701,777	-10,919
Wet process phosphoric acid	697,489-1,394,978	1,394,950	7,404	1,017,974	5,403
Ethylbenzene	430,913-861,826	861,827	-755	861,827	-755
Styrene	385,554-771,108	753,279	3,318	753,279	3,318
Acetic acid	4,082-8,165	8,165	268	0	0
Electric furnace phosphoric acid	697,489-1,394,978	na	na	0	0
HCl to phosphoric acid	697,489-1,394,978	na	na	0	0
New Acetic acid	4,082-8,165	na	na	8,165	8
SO_2 recovery from gypsum	902,208-1,804,417	na	na	0	0
S & SO_2 recovery from gypsum	451,526-903,053	na	na	0	0
Graphite & H_2 from CO_2 & CH_4	22,980-45,961	na	na	45,961	1,046
Syngas	6,966-13,933	na	na	13,933	894
Propene & H_2	20,896-41,791	na	na	0	0
Propene using CO_2	20,714-41,429	na	na	41,429	408
New Styrene	181,118-362,237	na	na	0	0
New methanol-Ushikoshi	239,890-479780	na	na	0	0
New methanol-Nerlov	240,000-480,000	na	na	0	0

Table 5.8. (Continued).

New methanol-Jun	239,763-479,526	na	na	0	0
New methanol-Bonivardi	238,724-477,449	na	na	0	0
Formic acid	38,974-77,948	na	na	77,948	14
Methylaimines	13,198-26,397	na	na	26,397	1,109
Ethanol	51,864-103,728	na	na	0	0
Dimethylether	22,727-45,454	na	na	0	0
Ammonia sale		10,227		0	
Ammnium Nitrate sale		218,441		105,057	
Urea sale		39,076		46,666	
Wet process phosphoric acid sale		13,950		10,180	
Ethylbenzene sale		0		0	
CO_2 vented		612,300		0	
Total energy requirement			4,028		7,689

The important results from Figure 5.4 and Table 5.8 are summarized in Table 5.9. From the results in Table 5.9, the following observations were made. For optimal solution, the profit increased about 24% from the base case to the optimal solution. The environmental costs decreased by 5.7%, and the sustainable costs increased by 5.5%. All of the carbon dioxide available from ammonia plant was consumed in the chemical production complex.

Table 5.9. Results for the Optimal Structure from Superstructure and Base Case, Case Study Two.

Property	**Base Case**	**Optimal Structure from Superstructure**
Profit	\$ 378 million/year	\$ 469 million/year
Environmental Cost	\$ 334 million/year	\$ 315 million/year
Sustainable Cost	\$ -18 million/year	\$ -17 million/year
CO_2 Utilized from NH_3 Plant	0.14 million tons/year	0.56 million tons/year
CO_2 Available from NH_3 Plant	0.61 million tons/year	0.00 million tons/year

D) Case Study Three – Consuming All of the CO_2 from Ammonia Plant Operating at Full Production Capacity

The System determined the optimum configuration of plants for consuming all of the carbon dioxide from the ammonia plant that operates at full production capacity. The optimal structure from the superstructure is shown in Figure 5.5, and a convenient way to show the new plants selected in the optimal structure is shown in Table 5.10. A table showing the flow rates of all streams among the plants in the optimal structure for the case study two is given in Appendix D.

Table 5.10. Plants in the Optimal Structure from Superstructure, Case Study Three.

Plants in the Base Case	**New Plants in the Optimal Structure**
Ammonia Nitric acid Ammonium nitrate Urea UAN Methanol Granular triple super phosphate (GTSP) MAP & DAP Power generation Contact process for Sulfuric acid Wet process for phosphoric acid Ethylbenzene **Plants Not in the Base Case** Acetic acid - standard method Styrene	Formic acid Acetic acid – new method Methylamines Graphite Hydrogen/Synthesis gas Propylene from CO_2 Propylene from propane dehydrogenation Styrene - new method DME **New Plants Not in the Optimal Structure** Electric furnace process for phosphoric acid HCl process for phosphoric acid SO_2 recovery from gypsum process S & SO_2 recovery from gypsum process Methanol - Bonivardi, et al., 1998 Methanol – Jun, et al., 1998 Methanol – Ushikoshi, et al., 1998 Methanol – Nerlov and Chorkendorff, 1999 Ethanol

Nine potentially new processes out of the eighteen that were integrated in the superstructure were selected by the System in the optimal structure, as shown in Table 5.10. The new processes for acetic acid plant and styrene replaced their corresponding commercial processes. All of the four new methanol plants were not selected in the optimal structure. The new processes for formic acid, methylamines, graphite, dimethyl ether (DME), and synthesis gas were selected by the System. Also, the two new processes for propylene were selected by the System. The new process for ethanol was

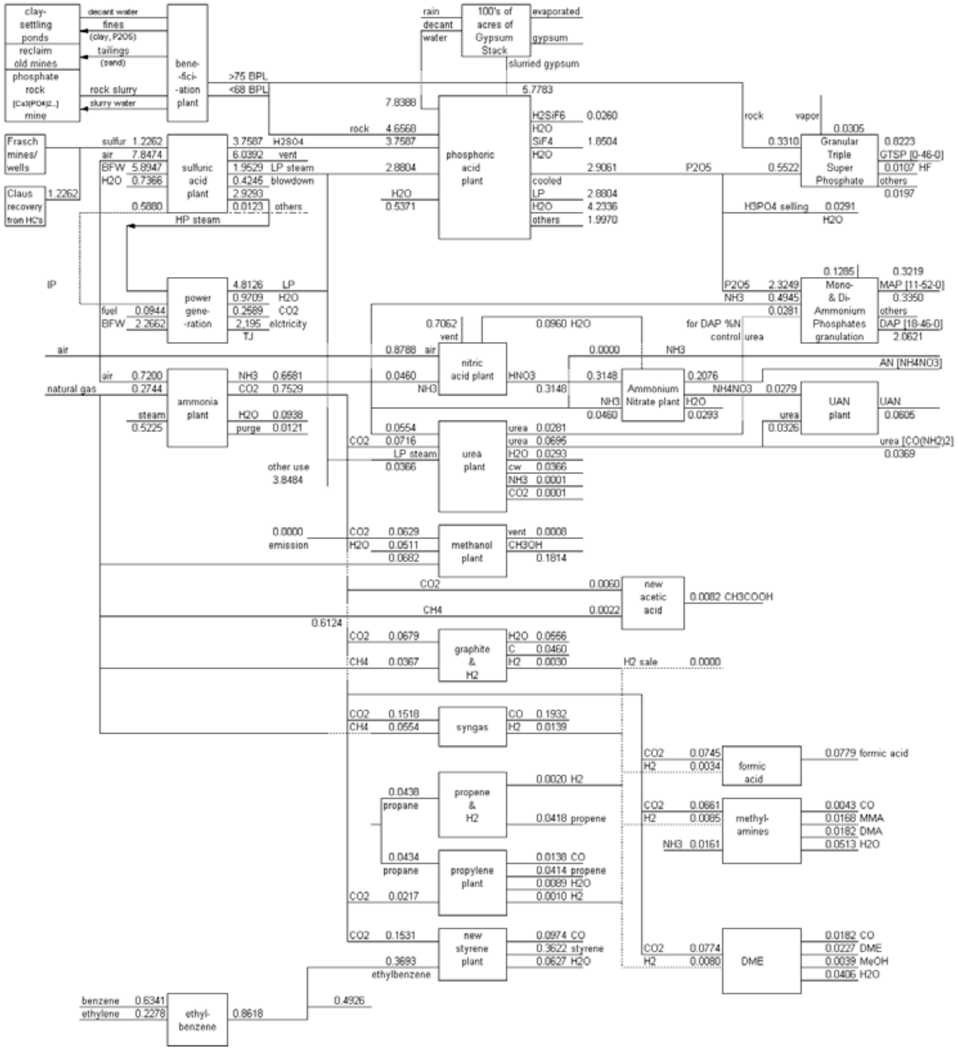


Figure 5.5. Chemical Production Complex Based on Plants in Lower Mississippi River Corridor, Optimal Structure from Superstructure, Case Study Three. Flow Rates Million TPY

not selected in the optimal structure. All the plants in the base case except for the standard acetic acid plant and styrene plant were selected in the optimal structure.

From the results, it was observed that all of the new processes present in the optimal structure except for methylamines and dimethyl ether (DME) were operated at full production capacities. A comparison of the results of the optimal structure with the results of the base case for the chemical production complex is shown in Table 5.11.

Table 5.11. Comparison of results for the Optimal Structure from Superstructure and Base Case, Case Study Three.

	Base case	Optimal structure
Profit (U.S.$/year)	378,325,617	459,608,034
Environmental cost (U.S.$/year)	334,403,783	368,257,342
Sustainability cost (U.S.$/year)	-18,039,196	-23,633,460

Plant name	**Capacity (t/year) (upper-lower bounds)**	**Capacity (t/year)**	**Energy Requirement (TJ/year)**	**Capacity (t/year)**	**Energy requirement (TJ/year)**
Ammonia	329,030-658,061	658,061	3,820	658,061	3,820
Nitric acid	0-178,547	178,525	-648	169,967	-617
Ammonium nitrate	113,398-226,796	226,796	117	215,924	108
Urea	49,895-99,790	99,790	128	97,626	125
Methanol	90,718-181,437	181,437	2,165	181,437	2,165
UAN	30,240-60,480	60,480	0	60,480	0
MAP	0-321,920	321,912		321,912	
DAP	0-2,062,100	2,062,100	2,137	2,062,100	2,137
GTSP	0-822,300	822,284	1,036	822,284	1,036
Contact process sulfuric acid	1,851,186-3,702,372	3,702,297	-14,963	3,702,297	-14,963
Wet process phosphoric acid	697,489-1,394,978	1,394,950	7,404	1,394,950	7,404
Ethylbenzene	430,913-861,826	861,827	-755	861,827	-756
Styrene	385,554-771,108	753,279	3,318	0	0
Acetic acid	0-8,165	8,165	268	0	0
Electric furnace phosphoric acid	697,489-1,394,978	na	na	0	0
HCl to phosphoric acid	697,489-1,394,978	na	na	0	0
New Acetic acid	0-8,165	na	na	8,165	8
SO2 recovery from gypsum	0-1,804,417	na	na	0	0

Table 5.11. (Continued).

S & SO2 recovery from gypsum	0-903,053	na	na	0	0
Graphite & H2 from CO2 & CH4	22,980-45,961	na	na	45,961	1,046
Syngas	6,966-13,933	na	na	13,933	894
Propene & H2	20,896-41,791	na	na	41,791	658
Propene using CO2	20,714-41,429	na	na	41,429	408
New Styrene	181,118-362,237	na	na	362,237	2,824
New methanol-Ushikoshi	239,890-479780	na	na	0	0
New methanol-Nerlov	240,000-480,000	na	na	0	0
New methanol-Jun	239,763-479,526	na	na	0	0
New methanol-Bonivardi	238,724-477,449	na	na	0	0
Formic acid	38,974-77,948	na	na	77,948	14
Methylaimines	13,198-26,397	na	na	16,763	704
Ethanol	51,864-103,728	na	na	0	0
Dimethylether	22,727-45,454	na	na	22,727	152
Ammonia sale		10,227		0	
Ammnium Nitrate sale		218,441		207,569	
Urea sale		39,076		36,912	
Wet process phosphoric acid sale		13,950		13,950	
Ethylbenzene sale		0		492,565	
CO2 vented		612,300		0	
Total energy requirement			4,028		7,169

In this case, all of the carbon dioxide from the ammonia plant was consumed, but the profit decreased when compared to that of case studies one and two. The profits in case studies one and two were \$529 million/year and \$469 million/year respectively, whereas the profit in case study three was \$460 million/year. This further decline in profit was expected as the ammonia plant was operated at full production capacity (658,000 metric tons/year), and thus more carbon dioxide was available when compared to the case study two. The production capacity of ammonia plant in case study was 491,000 metric tons of ammonia per year. In the case study two, 0.56 million tons of carbon dioxide per year were available from the ammonia plant, and the carbon dioxide available from ammonia plant in case study three was 0.75 million tons per year. To utilize all of this carbon dioxide, more new processes were selected by the System in the optimal structure. Thus, all of the carbon dioxide available from the ammonia plant (0.75 million tons per year) was consumed in methanol, urea, acetic acid, formic acid, styrene, methylamines, graphite, synthesis gas, propylene and dimethyl ether (DME) plants in the optimal structure.

The important results from Figure 5.5 and Table 5.11 are summarized in Table 5.12. From the results in Table 5.12, the following observations were made. For optimal solution from the superstructure, the profit increased by 21.7% compared to the base case. The environmental costs increased by 10.2%, and the sustainable costs decreased by 33.3%. All of carbon dioxide available from ammonia plant was consumed in the chemical production complex.

Table 5.12. Results for the Optimal Structure from Superstructure and Base Case, Case Study Three.

Property	**Base Case**	**Optimal Structure from Superstructure**
Profit	$ 378 million/year	$ 460 million/year
Environmental Cost	$ 334 million/year	$ 368 million/year
Sustainable Cost	$ -18 million/year	$ -24 million/year
CO_2 Utilized from NH_3 Plant	0.14 million tons/year	0.75 million tons/year
CO_2 Available from NH_3 Plant	0.61 million tons/year	0.00 million tons/year

E) Summary

The fourteen potentially new processes described in Chapter Four were integrated in the chemical complex using Chemical Complex and Cogeneration Analysis System. Also, four other processes that include two processes for phosphoric acid production and two processes for recovering sulfur and sulfur dioxide were included in the chemical complex. Three different cases studies to demonstrate the capability of the System were analyzed.

In the first case, the System determined the optimum configuration of plants based on economic, environmental and sustainable costs. For this case, the profit of the optimal structure increased by 40%, environmental costs increased by 4.5%, and sustainable costs decreased by 17% compared to the base case. The CO_2 vented from the ammonia plant decreased by 62.3%.

In the second study, the System determined the optimum configuration of plants for consuming all of the carbon dioxide from ammonia plant. In this case, the profit of the optimal structure increased by 24%, environmental costs decreased by 5.7%, and the sustainable costs increased by 5.5% when compared to the base case. Also, all of CO_2 available from the ammonia plant was consumed by the integration of the new processes in the chemical complex.

In the third study, the System determined the optimum configuration of plants for consuming all of the CO_2 available from ammonia plant operating at full production capacity. In this case, the profit of the optimal structure increased by 21.7%, environmental costs increased by 10.2%, and the sustainable costs decreased by 33.3% when compared to the base case. Also, all of the CO_2 available from the ammonia plant was consumed. The results of these three studies were summarized in Table 5.13.

Table 5.13. Comparison of the Results of Base Case to the optimal structures of the Three Case Studies.

Property	**Base Case**	**Case One**	**Case Two**	**Case Three**
Profit (million $/year)	378	529	469	460
Environmental Cost (million $/year)	334	349	315	368
Sustainable Cost (million $/year)	-18	-21	-17	-24
CO_2 Utilized from NH_3 Plant (million tons/year)	0.14	0.52	0.56	0.75
CO_2 Emitted from NH_3 Plant (million tons/year)	0.61	0.23	0.00	0.00

The conclusions for this research will be given in the next chapter. Recommendations for future work will also be made in the next chapter.

CHAPTER SIX: CONCLUSIONS AND SUGGESTIONS FOR FUTURE RESEARCH

The new processes for carbon dioxide utilization were integrated in the chemical complex using Chemical Complex and Cogeneration Analysis System. Three different case studies were evaluated and their results were analyzed in Chapter Five. The conclusions of this research and suggestions for future research are given in this chapter.

A) Conclusions

A new methodology was developed for identifying potentially new processes that use carbon dioxide as a raw material. The selection criteria includes process operating conditions like temperature and pressure, catalyst performance, cost of raw materials and demand for products. The thermodynamic feasibility of reactions involved and the by-products obtained were also considered.

Twenty new processes have been identified, and these were simulated using HYSYS. A value added economic analysis was evaluated for these processes using the results of the HYSYS simulations. Based on the value added economic model, fourteen potentially new processes were selected and integrated into the chemical production complex in the lower Mississippi River Corridor. These processes were integrated using Chemical Complex and Cogeneration Analysis System.

The Chemical Complex and Cogeneration Analysis System has been applied to an extended chemical production complex that determines the optimum configuration of plants from a superstructure. The value added economic model incorporated economic, environmental and sustainable costs. Three different case studies were evaluated to study the capability of the System. An optimum configuration of plants was determined with increased profit and reduced energy and emissions.

In the first case, the System determined the optimum configuration of plants based on economic, environmental and sustainable costs. For this case, the profit of the optimal structure increased by 40%, environmental costs increased by 4.5%, and sustainable costs decreased by 17% compared to the base case. The CO_2 vented from the ammonia plant decreased by 62.3%.

In the second study, the System determined the optimum configuration of plants for consuming all of the carbon dioxide from ammonia plant. In this case, the profit of the optimal structure increased by 24%, environmental costs decreased by 5.7%, and the sustainable costs increased by 5.5% when compared to the base case.

In the third study, the System determined the optimum configuration of plants for consuming all of the CO_2 available from ammonia plant operating at full production capacity. In this case, the profit of the optimal structure increased by 21.7%, environmental costs increased by 10.2%, and the sustainable costs decreased by 33.3% when compared to the base case.

The capability of the Chemical Complex and Cogeneration Analysis System has 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 complexes in the world for reduced emissions and energy savings. The System includes the program with users manual and tutorial, and these can be downloaded at no cost from the LSU Mineral Processing Research Institute's website www.mpri.lsu.edu. Also, all of the HYSYS simulations given in this research and the Chemical Complex Analysis program and users manual are available in the CD included with this thesis.

B) Suggestions for Future Research

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 plants in the Lower Mississippi River Corridor. Also, processes for fullerenes and carbon nanotubes can be evaluated for inclusion in the complex.

The flue gases from furnaces and boilers contain carbon dioxide. Typical sources of flue gas include gas-fired turbines, giving 3 mol % CO_2 and coal-fired plants, giving 10-12% CO_2 (Freguia, et al., 2003). This CO_2 from flue gas can be captured using amine scrubbing, and the capturing costs range from \$50-60 per ton of CO_2 captured (Simmonds, et al., 2002).

Some processes can directly use the flue gases from furnaces and boilers as a source of CO_2. However, the flue gas also contains SO_2 and NO_X that can act as catalyst poisons. Thus, the processes that can use the flue gases directly as a source of CO_2 and do not have problems of catalysts deactivation should be examined. Also, the processes that require pure CO_2 as a raw material can use pure CO_2 after being captured from the flue gas using amine scrubbing process.

Another option for the reduction of CO_2 emissions from the flue gases is the sequestration of CO_2. The costs for sequestering carbon dioxide in geological formations, oceans and natural systems have been summarized by Kim and Edmonds, 2000. They estimated the cost to range from \$120 to \$340 per metric ton of carbon equivalent. Also, they estimated that this cost would drop to \$50 per ton of carbon equivalent by 2015. Thus, to sequester the CO_2 from flue gases, pure CO_2 must be captured using amine scrubbing process and then have to be sequestered. The costs involved in capturing CO_2

from flue gases and the costs involved in CO_2 sequestering were already given in this section. Thus, a more effective way of reducing CO_2 emissions from flue gases would be to capture the CO_2 and then using it as a raw material to produce other industrially important products. Such potentially new processes should be examined in future work.

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APPENDIX A

COST ESTIMATION PROCEDURE FOR CARBON MONOXIDE

The price of carbon monoxide was estimated based on the fuel value of carbon monoxide, and the cost and heat of combustion of methane since the price for carbon monoxide was not available from the Chemical Market Reporter. The price ($/kg), and heats of combustion of methane (kcal/kg) and carbon monoxide are given in Table 4.24. The heats of combustion values for both the gases were taken from Perry's Chemical Engineers' Handbook. Using this information, the price of carbon monoxide was estimated in $/kg of CO. The procedure for estimating the price of CO is given below.

Table A.1. Heats of Combustion of Methane and Carbon Monoxide, and Price of Methane.

Property	**Methane**	**Carbon Monoxide**	**Source**
Heat of Combustion (kcal/kg)	13,265.1	2414.7	Perry's Chemical Engineers' Handbook
Selling Price ($/kg)	$0.172/kg, or $3.5/MBTU		http://www.repartners.org/renewables/recosts.htm

Price of methane = $0.172 /kg or $3.5 /MBTU

Heat of combustion of methane = 13265.1 kcal/kg-methane

$$\text{Price of methane in terms of \$/kcal} = \frac{\$\ 0.172\ /\text{kg}}{13265.1\ \text{kcal/kg-methane}}$$

$$= \$\ 1.2966 \times 10^{-5}\ /\text{kcal}$$

Heat of combustion of carbon monoxide = 2414.7 kcal/kg-CO

Price of CO in terms of $/kg-CO = ($ 1.2966 x 10^{-5} /kcal) (2414.7 kcal/kg-CO)

= $ 0.031 /kg-CO

Thus, the price of CO was estimated to be $ 0.031 /kg-CO.

APPENDIX B

COST ESTIMATION PROCEDURE FOR HYDROGEN

The price of hydrogen depends on the price of natural gas. Using the price of natural gas as \$3.5 per thousand cubic feet or million BTUs, the formula given by Kuehler, 2003 to compute the hydrogen price is:

$$\text{Hydrogen price (\$/Thousand SCF)} = \frac{[0.9(\text{natural gas price in \$/MBTU})]}{2} + 0.45$$

where, SCF is standard cubic feet

$$= 0.45(\text{natural gas price in \$/MBTU}) + 0.45$$

$$= (0.45 \times 3.5 + 0.45)\ \$/1000\ \text{ft}^3$$

$$= 0.0715\ \$/\text{m}^3$$

Thus, 1 m^3 of hydrogen costs \$ 0.0715

Kuehler, 2003, reported that the energy content (heat of combustion) of natural gas was 310 BTU/SCF. The density of hydrogen at standard state taken from Perry's Chemical Engineers' Handbook is 0.0898 kg/m^3. Using the density of hydrogen, the price of hydrogen can be represented in terms of \$/kg of H_2.

$$\text{Thus, the price of hydrogen} = \$\ \frac{0.0175}{0.0898}\ /\text{kg H}_2\ =\ \$\ 0.796/\ \text{kg H}_2$$

APPENDIX C

PROCEDURE FOR VALUE ADDED ECONOMIC ANALYSIS FOR A PROCESS

The procedure for evaluating a value added economic analysis for a process is discussed below with an example. The procedure is shown for the potentially new process for the production of acetic acid described by Taniguchi, et al., 1998. The calculations involve the raw material costs, product sales, and the energy costs. All the heat energy involved in the potentially new processes was assumed to be in the form of high-pressure (HP) steam. The conditions for HP steam are 47 bar, 260 ºC, and with a specific heat of 1.067 kcal/kg ºC.

The profit is calculated as the difference between the total product sales, raw material costs, and utility costs. The general equation for the calculation of value added economic profit is:

$$\text{Profit} = \Sigma \text{ Product Sales} - \Sigma \text{ Ram Material Costs} - \Sigma \text{ Utility Costs} \qquad (4.1)$$

Utilities include the cost of process steam, cooling water and electricity. In the value added economic analysis, the cost of steam and cooling water are included, but electricity is not included. Evaluating electricity requires a detailed process flow diagram with all pumps and compressors sized. Then the electrical requirements for the prime movers are summed.

The acetic acid process by Taniguchi, et al., 1998, described in Chapter Three is used to illustrate the evaluation. From the HYSYS simulation, the energy supplied to the process was 1,273 x 10^3 kJ/hr, and the process produced 933 kg/hr of acetic acid (Figure 4.12 and Table 4.13). Energy is supplied from the enthalpy of vaporization (ΔH_{vap}) of high-pressure (HP) steam, and the amount of HP steam required for this process is calculated as follows. The enthalpy of evaporation of HP steam at 260ºC is 1661.5 kJ/kg (Smith, et al., 1996).

HP steam required for this process = Energy from HYSYS/ ΔH_{vap} (kJ/hr)(kg/kJ)

$= 1{,}273 \times 10^3 / 1661.5$ kg/hr

$= 766$ kg/hr

From HYSYS flow sheet, Figure 4.12, the total energy liberated from this process was calculated to be 1,148 x 10^3 kJ/hr. Cooling water was heated from 30ºC and 50ºC (Turton, et al., 1998). The amount of cooling water required is given by the following equation.

$$q = mc_p\Delta T \tag{4.2}$$

Where, q = Energy absorbed, kcal/hr

m = Mass flow rate of cooling water, kg/hr

c_p = Specific heat of water, kJ/kg-ºC

ΔT = Change in temperature, ºC

The specific heat of water is 1 kcal/kgºC, and the difference in temperature is 20ºC since the water is entering at 30ºC and leaving at 50ºC. The value of q is the energy absorbed by the cooling water, and for acetic acid plant it was 1,148 x 10^3 kJ/hr. Substituting the values in Equation 4.2, the amount of cooling water required for this process was calculated to be 13,730 kg/hr.

The economic data used for this process is shown in Table 4.13, and it is repeated here for convenience.

Table 4.13. Economic Results for the HYSYS Simulated Process for the Production of Acetic Acid described by Taniguchi, et al., 1998.

Product/Raw Material	**Flow Rate from HYSYS Simulation (kg/h)**	**Cost/Selling Price ($/kg)**	**Source**
Carbon Dioxide	685	0.003	Hertwig, T. A., Private Communication, 2003
Methane	249	0.172	http://www.repartners.org/renewables/recosts.htm
Acetic Acid	933	1.034	Chemical Market Reporter, February 1, 2002
High Pressure Steam	766	0.00865	Turton, et al., 1998
Cooling Water	13,730	6.7×10^{-6}	Turton, et al., 1998
Value Added Profit	$ 913 / hr	97.9 cents/kg-acetic acid	

The product sales, raw material costs, cooling water costs, and the energy costs were calculated using the information provided in Table 4.12. The value added economic profit was calculated by substituting these values in equation 4.1.

HP Steam Cost = 766 x 0.00865 (kg/hr)($/kg)

= $ 6.63 /hr

Cooling Water Cost = 13,730 x 6.7×10^{-6} (kg/hr)($/kg)

= $ 0.092 /hr

Methane feed cost = 249 x 0.172 (kg/hr)($/kg)

= $ 42.83 /hr

Cost for delivering CO_2 from pipeline = 685 x 0.003 (kg/hr)($/kg)

= $ 2.06 /hr

Acetic acid sales = 933 x 1.034 (kg/hr)($/kg)

= $ 964.72 /hr

Total Profit, $/h = $ (- 6.63 – 0.092 – 42.83 – 2.06 + 964.72) /hr = $ 913 /hr

Total Profit, \$/kg- acetic acid = 913 / 933 (\$/hr)/(kg-acetic acid/hr)

= 97.9 cents/kg-acetic acid

Thus, the value added economic profit for this potentially new process was 97.9 cents per kg of acetic acid. This profit was based on a selling price of \$1.03 per kg of acetic acid (Chemical Market Reporter, 2002), as shown in Table 4.13. The above economic model considered only the raw material costs, product sales, cooling water costs, and the energy costs. The other operating costs, and a return on investment were not included. Thus, the profit expected from the value added economic model decreases if all the other operating costs were included.

A list of current selling prices of products and raw material costs for various chemicals used in this research was given in Table 4.25.

Table C.1. Product Prices and Raw Material Costs.

Product/Raw Material	**Cost/Selling Price (\$/kg)**	**Source**
Methane	0.172	http://www.repartners.org/renewables/recosts.htm
Hydrogen	0.796	Appendix B
Methanol	0.300	Chemical Market Reporter, 2003
Graphite	0.882	Camford Chemical Prices, 2000
HP Steam	0.00865	Turton, et al., 1998
Cooling Water	6.7×10^{-6}	Turton, et al., 1998
Carbon Monoxide	0.031	Appendix A
Dimethyl Ether	0.946	http://www.che.cemr.wvu.edu/publications/projects/dimethyl/dme-b.pdf
Carbon Dioxide	0.003	Hertwig, T. A., Private Communication, 2003
Formic Acid	0.690	Chemical Market Reporter, April 1, 2002
Mono-Methylamine	1.606	Chemical Market Reporter, 2000
Di-Methylamine	1.606	Chemical Market Reporter, 2000
Ammonia	0.150	Chemical Market Reporter, February 4, 2002
Ethanol	0.670	Chemical Market Reporter, 2002
Acetic Acid	1.034	Chemical Market Reporter, 2002
Ethylbenzene	0.551	Chemical Market Reporter, 2002
Styrene	0.705	Chemical Market Reporter, 2002
Propane	0.163	C & EN, June 2003, p.15
Propylene	0.240	C & EN, June 2003, p.15

APPENDIX D

STREAM FLOW RATES AMONG PLANTS IN THE CHEMICAL 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	1,226,200	Sulfuric acid	3,758,700
	Air	7,847,400	Vent	6,039,200
	Boiler feed water	5,894,700	LP steam	1,952,900
	H_2O	736,600	Blowdown	424,500
			HP steam	2,929,300
			IP steam	588,000
			Others	12,300
Wet process phosphoric acid	Decant water	7,838,800	H_2SiF_6 & H_2O	26,000
	Phosphate rock	4,656,800	SiF_4 & H_2O	1,850,400
	Sulfuric acid	3,758,700	P_2O_5	2,906,100
	LP steam	2,880,400	Cooled LP steam	2,880,400
	H_2O	537,100	H_2O	4,233,600
			Others	1,997,000
GTSP	Phosphate rock	331,000	GTSP	822,300
	P_2O_5	552,200	HF	10,700
			Vapor	30,500
			Others	19,700
MAP & DAP	P_2O_5	2,324,900	MAP	321,900
	NH_3	494,500	DAP	2,062,100
	Urea	28,100	H_2O	128,500
			Others	335,000
Power generation	HP steam	2,929,300	LP steam	3,899,400
	IP steam	588,000	H_2O	848,600
	Fuel (methane)	51,300	CO_2	140,600
	Boiler feed water	1,230,700	Electricity	1,821 (TJ)
Ammonia	Air	720,000	NH_3	658,100
	Natural gas	274,400	CO_2	752,900
	Steam	522,500	H_2O	93,800
			Purge	12,100
Nitric acid	Air	923,100	HNO_3	330,600
	NH_3	48,400	Vent	741,700
	H_2O	100,900		
Methanol	CO_2	62,900	Methanol	181,400
	H_2O	51,100	Vent	800
	Natural gas	68,200		

Table D.1. (Continued)

Ammonium nitrate	HNO_3	330,600	NH_4NO_3	246,300
	NH_3	48,300	H_2O	132,600
UAN	NH_4NO_3	27,900	UAN	60,500
	Urea	32,600		
Urea	NH_3	56,700	Urea	99,800
	CO_2	73,200	H_2O	29,900
	LP steam	37,400	Cooling water	37,400
			NH_3	100
			CO_2	100
Acetic acid	CO_2	4,500	Acetic acid	8,200
	Methanol	4,400	H_2O	1,200
	CH_4	500		
Ethylbenzene	Benzene	634,000	Ethylbenzene	861,800
	Ethylene	227,800		
Styrene	Ethylbenzene	861,800	Styrene	753,300
			Fuel gas	35,500
			Toluene	6,700
			C	15,600
			Benzene	50,700

Table D.2. Stream Flow Rates Among Plants in Optimal Structure from Superstructure, Case Study One.

Plant Name	**Entering Streams**	**Flow Rate (metric tons/year)**	**Leaving Streams**	**Flow Rate (metric tons/year)**
Contact process sulfuric acid	Sulfur	1,226,200	Sulfuric acid	3,758,700
	Air	7,847,400	Vent	6,039,200
	Boiler feed water	5,894,700	LP steam	1,952,900
	H_2O	736,600	Blowdown	424,500
			HP steam	2,929,300
			IP steam	588,000
			Others	12,300
Wet process phosphoric acid	Decant water	7,838,800	H_2SiF_6 & H_2O	26,000
	Phosphate rock	4,656,800	SiF_4 & H_2O	1,850,400
	Sulfuric acid	3,758,700	P_2O_5	2,906,100
	LP steam	2,880,400	Cooled LP steam	2,880,400
	H_2O	537,100	H_2O	4,233,600
			Others	1,997,000
GTSP	Phosphate rock	331,000	GTSP	822,300
	P_2O_5	552,200	HF	10,700
			Vapor	30,500
			Others	19,700
MAP & DAP	P_2O_5	2,324,900	MAP	321,900
	NH_3	494,500	DAP	2,062,100
	Urea	28,100	H_2O	128,500
			Others	335,000
Power generation	HP steam	2,929,300	LP steam	4,701,200
	IP steam	588,000	H_2O	956,000
	Fuel (methane)	89,200	CO_2	244,500
	Boiler feed water	2,139,900	Electricity	2,149 (TJ)
Ammonia	Air	720,000	NH_3	658,100
	Natural gas	274,400	CO_2	752,900
	Steam	522,500	H_2O	93,800
			Purge	12,100
Nitric acid	Air	923,100	HNO_3	330,600
	NH_3	48,400	Vent	741,700
	H_2O	100,900		
Ammonium nitrate	HNO_3	330,600	NH_4NO_3	246,300
	NH_3	48,300	H_2O	132,600
Methanol	CO_2	62,900	Methanol	181,400
	H_2O	51,100	Vent	800
	Natural gas	68,200		
UAN	NH_4NO_3	27,900	UAN	60,500
	Urea	32,600		

Table D.2. (Continued).

Urea	NH_3 CO_2 LP steam	41,600 53,700 27,400	Urea H_2O Cooling water NH_3 CO_2	73,200 22,000 27,400 0 100
Ethylbenzene	Benzene Ethylene	634,000 227,800	Ethylbenzene	861,800
Styrene	Ethylbenzene	861,800	Styrene Fuel gas Toluene C Benzene	753,300 35,500 6,700 15,600 50,700
New acetic acid	CO_2 CH_4	6,000 2,200	Acetic acid	8,200
Graphite	CO_2 CH_4	67,900 36,700	H_2O C Hydrogen	55,600 46,000 3,000
Synthesis gas	CO_2 CH_4	150,000 54,700	CO Hydrogen	191,000 13,800
Formic acid	CO_2 Hydrogen	74,500 3,400	Formic acid	77,900
Methylamines	CO_2 Hydrogen NH_3	104,100 13,300 25,300	CO MMA DMA H_2O	6,800 26,400 28,700 80,800

Table D.3. Stream Flow Rates Among Plants in Optimal Structure from Superstructure, Case Study Two.

Plant Name	Entering Streams	Flow Rate (metric tons/year)	Leaving Streams	Flow Rate (metric tons/year)
Contact process sulfuric acid	Sulfur	894,800	Sulfuric acid	2,742,900
	Air	5,726,700	Vent	4,407,200
	Boiler feed water	4,301,700	LP steam	1,425,100
	H_2O	537,500	Blowdown	309,800
			HP steam	2,137,700
			IP steam	429,100
			Others	8,900
Wet process phosphoric acid	Decant water	5,720,400	H_2SiF_6 & H_2O	18,900
	Phosphate rock	3,398,400	SiF_4 & H_2O	1,350,400
	Sulfuric acid	2,742,900	P_2O_5	2,906,100
	LP steam	2,102,000	Cooled LP steam	2,120,800
	H_2O	392,00	H_2O	3,089,500
			Others	1,457,300
GTSP	Phosphate rock	241,500	GTSP	600,100
	P_2O_5	402,900	HF	7,800
			Vapor	22,300
			Others	14,300
MAP & DAP	P_2O_5	1,696,600	MAP	234,900
	NH_3	360,900	DAP	1,504,800
	Urea	20,500	H_2O	93,800
			Others	244,500
Power generation	HP steam	2,137,700	LP steam	4,241,900
	IP steam	429,100	H_2O	806,400
	Fuel (methane)	103,400	CO_2	283,500
	Boiler feed water	2,481,500	Electricity	1,873 (TJ)
Ammonia	Air	537,500	NH_3	491,200
	Natural gas	204,900	CO_2	562,00
	Steam	390,000	H_2O	70,000
			Purge	9,000
Nitric acid	Air	461,600	HNO_3	165,300
	NH_3	24,200	Vent	370,900
	H_2O	50,400		
Ammonium nitrate	HNO_3	165,300	NH_4NO_3	133,000
	NH_3	24,100	H_2O	56,500
Methanol	CO_2	62,900	Methanol	181,400
	H_2O	51,100	Vent	800
	Natural gas	68,200		
UAN	NH_4NO_3	27,900	UAN	60,500
	Urea	32,600		

Table D.3. (Continued).

Urea	NH_3	56,700	Urea	99,800
	CO_2	73,200	H_2O	29,900
	LP steam	37,400	Cooling water	37,400
			NH_3	100
			CO_2	100
Ethylbenzene	Benzene	634,000	Ethylbenzene	861,800
	Ethylene	227,800		
Styrene	Ethylbenzene	861,800	Styrene	753,300
			Fuel gas	35,500
			Toluene	6,700
			C	15,600
			Benzene	50,700
New acetic acid	CO_2	6,000	Acetic acid	8,200
	CH_4	2,200		
Graphite	CO_2	67,900	H_2O	55,600
	CH_4	36,700	C	46,000
			Hydrogen	3,000
Synthesis gas	CO_2	151,800	CO	193,200
	CH_4	55,400	Hydrogen	13,900
Formic acid	CO_2	74,500	Formic acid	77,900
	Hydrogen	3,400		
Methylamines	CO_2	104,100	CO	6,800
	Hydrogen	13,300	MMA	26,400
	NH_3	25,300	DMA	28,700
			H_2O	80,800
Propylene from CO_2	Propane	43,400	CO	13,800
	CO_2	21,700	Propylene	41,400
			H_2O	8,900
			Hydrogen	1,000

Table D.4. Stream Flow Rates Among Plants in Optimal Structure from Superstructure, Case Study Three.

Plant Name	**Entering Streams**	**Flow Rate (metric tons/year)**	**Leaving Streams**	**Flow Rate (metric tons/year)**
Contact process sulfuric acid	Sulfur	1,226,200	Sulfuric acid	3,758,700
	Air	7,847,400	Vent	6,039,200
	Boiler feed water	5,894,700	LP steam	1,952,900
	H_2O	736,600	Blowdown	424,500
			HP steam	2,929,300
			IP steam	588,000
			Others	12,300
Wet process phosphoric acid	Decant water	7,838,800	H_2SiF_6 & H_2O	26,000
	Phosphate rock	4,656,800	SiF_4 & H_2O	1,850,400
	Sulfuric acid	3,758,700	P_2O_5	2,906,100
	LP steam	2,880,400	Cooled LP steam	2,880,400
	H_2O	537,100	H_2O	4,233,600
			Others	1,997,000
GTSP	Phosphate rock	331,000	GTSP	822,300
	P_2O_5	552,200	HF	10,700
			Vapor	30,500
			Others	19,700
MAP & DAP	P_2O_5	2,324,900	MAP	321,900
	NH_3	494,500	DAP	2,062,100
	Urea	28,100	H_2O	128,500
			Others	335,000
Power generation	HP steam	2,929,300	LP steam	4,812,600
	IP steam	588,000	H_2O	970,900
	Fuel (methane)	9,440	CO_2	258,900
	Boiler feed water	2,266,200	Electricity	2,195 (TJ)
Ammonia	Air	720,000	NH_3	658,100
	Natural gas	274,400	CO_2	752,900
	Steam	522,500	H_2O	93,800
			Purge	12,100
Nitric acid	Air	878,800	HNO_3	314,800
	NH_3	46,000	Vent	706,200
	H_2O	96,000		
Ammonium nitrate	HNO_3	314,800	NH_4NO_3	235,500
	NH_3	46,00	H_2O	125,300
Methanol	CO_2	62,900	Methanol	181,400
	H_2O	51,100	Vent	800
	Natural gas	68,200		
UAN	NH_4NO_3	27,900	UAN	60,500
	Urea	32,600		

Table D.4. (Continued).

Urea	NH_3	55,400	Urea	97,600
	CO_2	71,600	H_2O	29,300
	LP steam	36,600	Cooling water	36,600
			NH_3	100
			CO_2	100
Ethylbenzene	Benzene	634,100	Ethylbenzene	861,800
	Ethylene	227,800		
Styrene – new method	CO_2	153,100	CO	97,400
	Ethylbenzene	369,300	Styrene	362,200
			H_2O	62,700
New acetic acid	CO_2	6,000	Acetic acid	8,200
	CH_4	2,200		
Graphite	CO_2	67,900	H_2O	55,600
	CH_4	36,700	C	46,000
			Hydrogen	3,000
Synthesis gas	CO_2	151,800	CO	193,200
	CH_4	55,400	Hydrogen	13,900
Formic acid	CO_2	74,500	Formic acid	77,900
	Hydrogen	3,400		
Methylamines	CO_2	66,100	CO	4,300
	Hydrogen	8,500	MMA	16,800
	NH_3	16,100	DMA	18,200
			H_2O	51,300
Propylene from propane dehydrogenation	Propane	43,800	Propylene	41,800
			Hydrogen	2,000
Propylene from CO_2	CO_2	21,700	CO	13,800
	Propane	43,400	Propylene	41,400
			H_2O	8,900
			Hydrogen	1,000
DME	CO_2	77,400	CO	18,200
	Hydrogen	8,000	DME	22,700
			Methanol	3,900
			H_2O	40,600

VITA

Sudheer Indala was born on August 28, 1978, in Visakhapatnam, India. He completed his secondary education from Gowtam Junior College, Vijayawada, India, in May 1996. He received the degree of Bachelor of Technology in Chemical Engineering from Andhra University, Visakhapatnam, India, in May 2001. Later in August 2001, he was enrolled in the Department of Chemical Engineering at Louisiana State University, Baton Rouge, Louisiana, to attend graduate school. He is presently a candidate for the degree of Master of Science in Chemical Engineering.