Identifying and Developing New, Carbon Dioxide Consuming Processes

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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.

About 100 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.

The criteria for process selection included operating conditions, energy requirement for reactions, $)H_o$ and equilibrium conversion based on Gibbs free energy, $)G_o$; 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.

About 20 potential processes were identified as candidates for new energy efficient and environmentally acceptable plants. From these, three of the more promising were selected for further evaluation using HYSYS. These processes were hydrogenation of propane, styrene from ethyl benzene and carbon dioxide, and methanol from hydrogenation of carbon dioxide.

A base case of existing plants a chemical production complex in the lower Mississippi river corridor was developed that included ten multiple plant production units. The System was used with the base case and potentially new plants for carbon dioxide, and an optimal configuration of plants was determined based on economic, environmental and sustainable costs. A comparison of the base case with the optimal one showed that the profit increased about 49%, the environmental cost increased about 21%, and sustainable costs decreased about 9.36%.

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.

Introduction

The domestic chemical industry is an integral part of the nation's economy and consistently contributes 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 high energy costs, inefficient power generation and greenhouse gas emission constraints (Sikdar, 2003).

The use of a regional methodology for energy conservation, pollution prevention and conversion of greenhouse gases to products will assist in overcoming these limitations. The Chemical Complex and Cogeneration Analysis System is an advanced technology for energy conservation and pollution prevention to determine the best configuration of plants in a chemical complex based the AIChE Total Cost Assessment(TCA) for economic, energy, environmental and sustainable costs and incorporates EPA Pollution Index methodology (WAR) algorithm. It is used to examine chemical complex energy use and determines the best energy use based on economics, energy efficiency, regulatory emissions and environmental impacts from greenhouse gas emissions. The System includes the program with users' manuals and tutorials. They can be downloaded at no cost from the LSU Mineral Processing Research Institute's web site www.mpri.lsu.edu (Xu, et al., 2003).

This System is to be used by corporate engineering groups for regional economic, energy, environmental and sustainable development planning to design energy-efficient and environmentally acceptable plants and new products from greenhouse gases in chemical production complexes. With this System, engineers will have a new capability to consider projects in depths significantly beyond current capabilities. They will be able to convert the company's goals and capital into viable projects that are profitable and meet energy and environmental requirements by developing and applying a regional methodology for cogeneration, and conversion of greenhouse gases to saleable products. In Table 1 a list of some of the chemical complexes in the world, and the System could be applied to these complexes.

This technology is being applied to a key part of the chemical production complex in the lower Mississippi River corridor shown in Figure 1 (Peterson, 1999). This complex contains over 150 chemical plants that consume about 1.0 quad ($1x10^{15}$ Btu/yr) of energy and generate about 215 million pounds of pollutants annually. Ammonia plants in this complex produce an excess of 0.65 million tons per year of high quality carbon dioxide that is being exhausted to the atmosphere. New catalytic processes that converts carbon dioxide and methane can use some of this excess, and results using the System showed that replacing the conventional acetic acid process in the existing complex with the new process gave a potential savings of $750,000 per year for steam, 275 trillion BTUs per year in energy, and 3.5 tons per year in NO_x and 49,100 tons per year in carbon dioxide

Table 1 Some Chemical Production Complexes in 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) • BASF in Ludwigshafen (Germany)	• Largest petrochemical complex in Europe and world wide second only to Houston, Texas • Europe's largest chemical factory complex
Asia	• The Singapore petrochemical complex in Jurong Island (Singapore) • 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) • Jamnagar refinery and petrochemical complex (India) • Sabic company based in Jubail Industrial City (Saudi Arabia) • Petrochemical complex in Yanbu (Saudi Arabia) • Equate (Kuwait)	• World's third largest oil refinery center • Largest petrochemical complex in Asia • World's largest polyethylene manufacturing site • 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

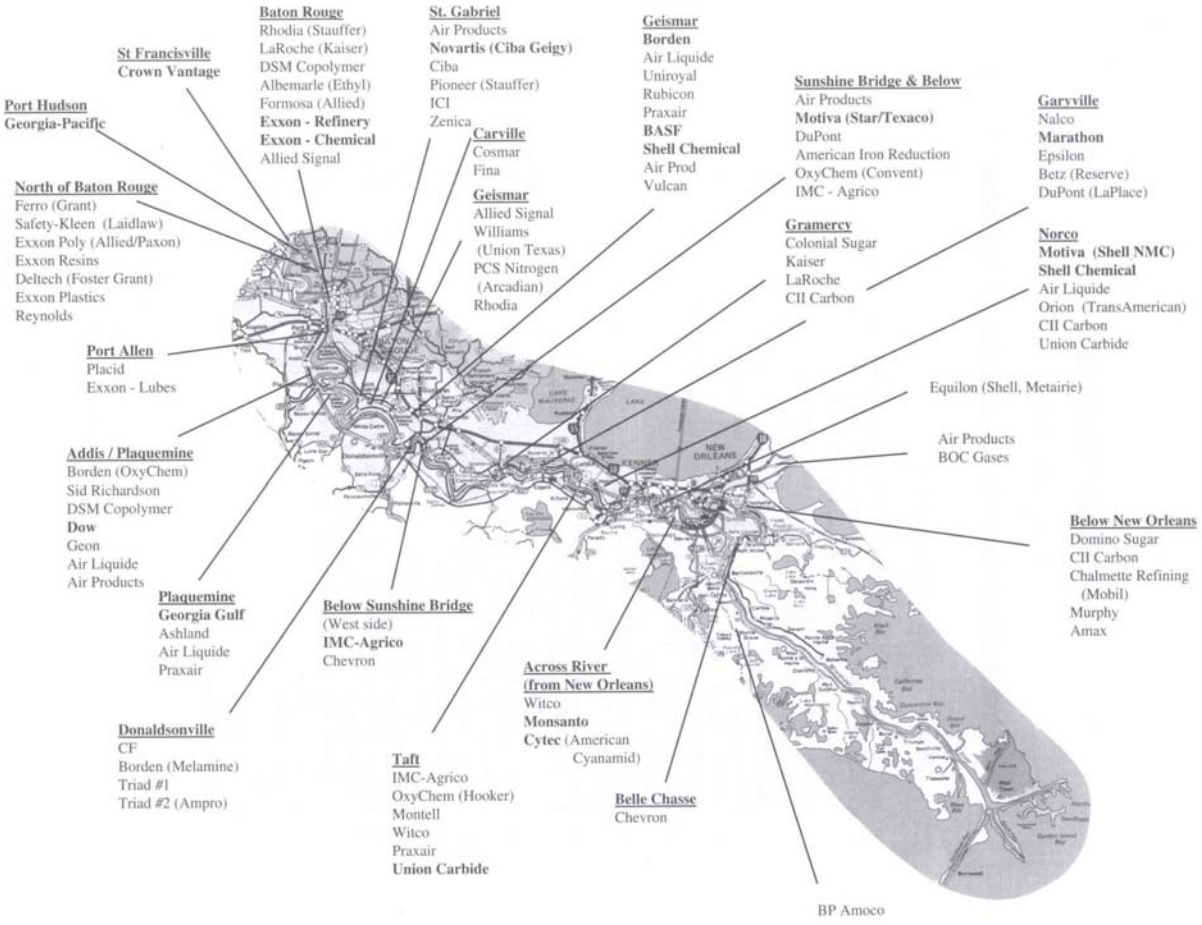


Figure 1 Chemical Plants in the Lower Mississippi River Corridor, from Peterson, 1999.

emissions (Xu, et al., 2002).

In Table 2 a summary is given of carbon dioxide emissions worldwide, by nations, by the U.S. by U.S. industry and the chemicals, coal and refining industries. Also, 30 million metric tons carbon equivalent per year or 110 million metric tons of CO_2 per year are used for chemical synthesis. However, there is excess of high purity CO_2 that is discharged to the atmosphere, mainly from ammonia plants.

Table 2 Carbon Dioxide Emissions and Utilizations

(Million Metric Tons Carbon Equivalent Per Year)

CO_2 emissions and utilization		Reference
Total CO_2 added to atmosphere		IPCC (1995)
Burning fossil fuels	5,500	
Deforestation	1,600	
Total worldwide CO_2 from consumption and flaring of fossil fuels		EIA (2002)
United States	1,526	
China	792	
Russia	440	
Japan	307	
All others	3,258	
U.S. CO_2 emissions		Stringer (2001)
Industry	630	
Buildings	524	
Transportation	473	
Total	1,627	
U.S. industry (manufacturing)		EIA (2001)
Petroleum, coal products and chemicals	174.8	
Chemical and refinery (BP)		McMahon (1999)
Combustion and flaring	97%	
Noncombustion direct CO_2 emission	3%	
Chemical production 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)

To highlight the practicality of the study complex and of the Chemical Complex Analysis System that it serves, carbon dioxide pipelines are discussed next. Multi-mile inter-plant pipelines are a useful way of getting a bigger complex with more opportunities for optimizing. Thousand-mile gas-and-oil pipelines have been around for years, delivering crude oil to refineries and fuel to the nation. Water is piped hundreds of miles to thirsty cities. Ammonia plants, industrial users, and distribution terminals on the west bank of the Mississippi River are connected by a 1,100-mile ammonia pipeline. Besides cutting transportation costs and chances for hazardous spills, this line serves to better balance incremental supply vs incremental demand. This balancing is even more valuable when one supplying or one using plant is down for maintenance. Louisiana has at least two multi-mile pipelines for hydrogen, a hazardous material that is difficult to store many pounds of in a vessel either for on-site storage or for transport.

There are multi-mile pipelines for often-wasted carbon dioxide as well as for the seldom-wasted hydrogen. Urea, methanol, and a few other processes rely on a reliable source of carbon dioxide.

- For years, Ashland Chemical's methanol plant ran on carbon dioxide piped from an ammonia plant about 13 miles away.
- At least two across-the-fence carbon dioxide pipeline have been built to keep a urea plant and a methanol plant running while its normal-carbon dioxide-source ammonia plant was down for maintenance.
- The 183-mile Denbury carbon dioxide pipeline distributes carbon dioxide from a volcanic formation near Jackson MS to many MS oilfields and to some chemical production. This line extends into Louisiana and could be a key in sustaining urea, methanol, etc. production in LA. (Louisiana methanol production has stopped for other reasons, mostly the demise of MTBE that was produced from methanol.)
- There are many other oilfield-servicing carbon dioxide pipelines in the MS-UT-NM triangle. Twelve of these lines total total 1,016 miles. The carbon dioxide source for these lines is 'high-carbon dioxide-content natural gas'.

If ammonia production resumes if natural gas prices ever stabilize at lower levels, the Denbury pipeline, with the oil wells it serves, would be another way of taking ammonia-byproduct carbon dioxide out of the atmosphere. This goes beyond the goal of the current-study-complex to convert carbon dioxide into useful products. This study acknowledges that the life cycle of some of those products ends up as atmospheric carbon dioxide anyway. This 'penalty' and the 'benefit' of injecting carbon dioxide in oil wells could each, however, be suitably valued via the Chemical Complex Analysis System.

When ammonia plants, as the primary source of carbon dioxide, are shut down, as today, with high natural gas prices, the urea, etc. producers have to scramble for alternate sources of carbon

dioxide. As with most projects, more deals have been considered than have been completed. The dealing continues, however. Considerations include the cost of land purchases for pipeline right-of-way and the long-term availability of the carbon dioxide source. Tying into the MS-LA volcanic-carbon dioxide pipeline is an interesting option that is independent of ammonia production.

Greenhouse Gases as Raw Materials

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, Inui, et al., 1998, Sullivan, 1993 and Inoue and Yamazaki, 1982). The diagram Figure 2 from Creutz and Fujita, 2000. 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, e.g., in the dehydrogenation of ethylbenzene to styrene. For example, commercially important products can be obtained from hydrogenation and hydrolysis of carbon dioxide, and these include methanol, ethanol, methane, ethylene, formic acid, acetic acid, adipic acid and graphite. Also, carbon dioxide can be used to produce methyl amines and as a building block for isocynates supplanting phosgene.

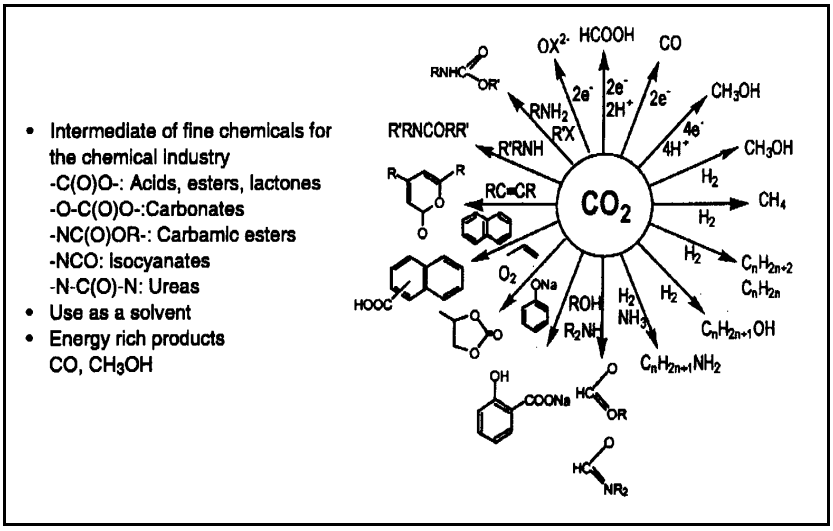


Figure 2 Utilization of Carbon Dioxide in Synthetic Chemistry, from Creutz and Fujita, 2000.

In Figure 3, carbon dioxide reactions are categorized by industrially important products. Hydrogenation reactions produce alcohols, hydrocarbon synthesis reactions produce paraffins and olefins, and amine synthesis 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.

For the reactions shown in Figure 3, there are nearly 100 published articles of laboratory experiments for new methods and catalysts to produce these commercially important products (Hertwig, et al., 2003). An important reaction is the direct catalytic reaction of carbon dioxide and

methane to produce acetic acid, and this reaction has been used in a new process that was evaluated using the Chemical Complex and Cogeneration Analysis System (Xu, et al., 2002).

Figure 3. Some Catalytic Reactions of CO_2 from Various Sources, Hertwig, et al., 2003

Hydrogenation

$CO_2 + 3H_2$! $CH_3OH + H_2O$	methanol
$2CO_2 + 6H_2$! $C_2H_5OH + 3H_2O$	ethanol
$CO_2 + H_2$! $CH_3\text{-}O\text{-}CH_3$	dimethyl ether

Hydrocarbon Synthesis

$CO_2 + 4H_2$! $CH_4 + 2H_2O$	methane and higher HC
$2CO_2 + 6H_2$! $C_2H_4 + 4H_2O$	ethylene and higher olefins

Carboxylic Acid Synthesis

$CO_2 + H_2$! HC=O-OH	formic acid
$CO_2 + CH_4$! $CH_3\text{-}C{=}O\text{-}OH$	acetic acid

Graphite Synthesis

$CO_2 + H_2$! $C + H_2O$

CH_4 ! $C + H_2$

$CO_2 + 4H_2$! $CH_4 + 2H_2O$

Hydrolysis and Photocatalytic Reduction

$CO_2 + 2H_2O$! $CH_3OH + O_2$

$CO_2 + H_2O$! $HC{=}O\text{-}OH + 1/2O_2$

$CO_2 + 2H_2O$! $CH_4 + 2O_2$

Other Reactions

CO_2 + ethylbenzene ! styrene

dehydrogenation of propane

$CO_2 + C_3H_8$! $C_3H_6 + H_2 + CO$

reforming

$CO_2 + CH_4$! $2CO + H_2$

Amine Synthesis

methyl amine and higher amines

$CO_2 + 3H_2 + NH_3$! $CH_3\text{-}NH_2 + 2H_2O$

New, energy-efficient and environmentally acceptable, catalytic processes were identified from published articles of laboratory experiments described above that can use excess high purity carbon dioxide as a raw material. A methodology has been developed to select these potentially new processes for incorporation into the existing chemical complex.

The selected processes are simulated as industrial scale processes to estimate the process economics and energy requirements. The simulations of these processes are done using HYSYS. These potentially new processes are included in the Chemical Complex and Cogeneration Analysis System, and it is used to evaluate the energy and greenhouse gas reductions in the chemical production complex in the lower Mississippi River Corridor. New processes are compared to the existing commercial processes, when appropriate.

The criteria for process selection included operating conditions, energy requirement for reactions, ΔH_o and equilibrium conversion based on Gibbs free energy, ΔG_o; 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.

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, and these estimates were used in screening potential processes.

Table 3. 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

Thermodynamic feasibility of reactions was used as a criterion for selection of new processes. using the heat of reaction (ΔH^o), and the standard Gibbs free energies (ΔG^o) of reaction. 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, and there is a corresponding

energy cost. If a process has an exothermic reaction, then energy is released, which can be used effectively else where. Such a process has the potential to reduce the total energy costs in a chemical complex.

For the cost of raw materials with CO_2 hydrogenation reactions, the conversion can be increased if H_2/CO_2 ratio is high (3-4). These processes require hydrogen, and hydrogen is an expensive raw material. If H_2 is formed as a by-product in a new process added to the complex, it could be a source for expensive hydrogen. For example, a new process for propylene manufacture from propane produces hydrogen as a by-product. This new process could provide hydrogen that could be used in other processes.

In summary, about 20 processes were identified and potential candidates for new energy efficient and environmentally acceptable plants. From these three of the more promising were selected for further evaluation using HYSYS. These processes were hydrogenation of propane, styrene from ethyl benzene and carbon dioxide, and methanol from hydrogenation of carbon dioxide. The HYSYS simulation and evaluation of these three processes are discussed below.

Potential Processes for Carbon Dioxide

Propane Dehydrogenation: 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 and is given below.

$$2C_3H_8 + CO_2 \div 2C_3H_6 + CO + H_2O + H_2 \quad) H^o = 289 \text{ kJ/mol}, \ ) G^o = 201 \text{ kJ/mol}.$$

This reaction is endothermic and 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. 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).

The flow diagram of the HYSYS simulation for this study is shown in Figure 4. The value added economic model gave a profit of 14 cents per pound of propylene for a 60,500 pound per hour plant. The energy required for this potentially new process estimated from HYSYS flow sheet was 655 kJ/kg propylene. This potentially new process was integrated into the chemical production complex using Chemical Complex and Cogeneration Analysis System.

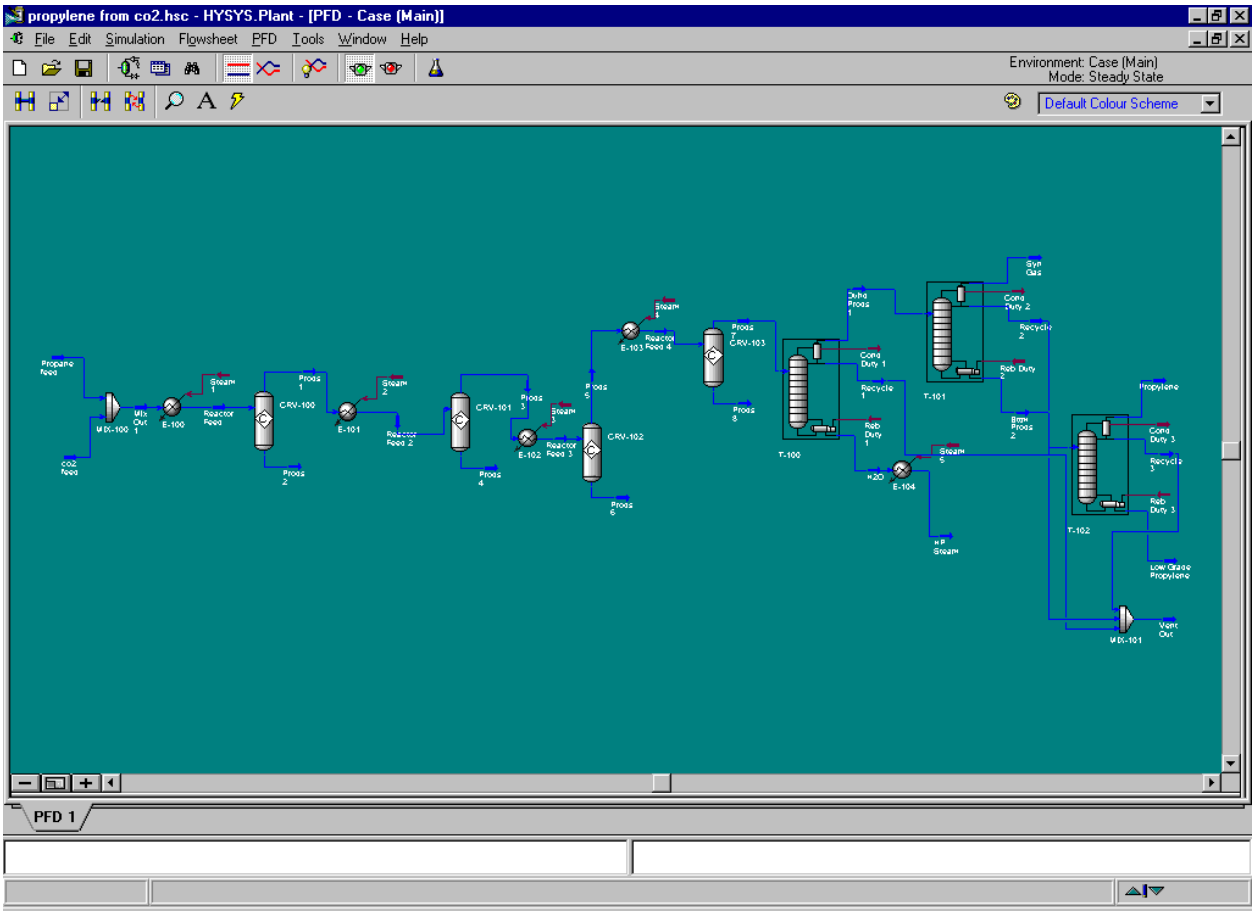


Figure 4. HYSYS Simulation of Propylene Production Process.

Styrene Production: 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. During the reaction, carbon dioxide, corresponding to the amount of styrene produced, was reduced to carbon monoxide to give water. Styrene was produced according to the following reaction.

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

The flow sheet of the HYSYS simulation based on this experimental study is shown in Figure 5. The value added economic model gave a profit of 2.6 cents per pound of styrene for a 30,000 pound per hour plant. Using HYSYS flow sheet, the energy required for this potentially new process

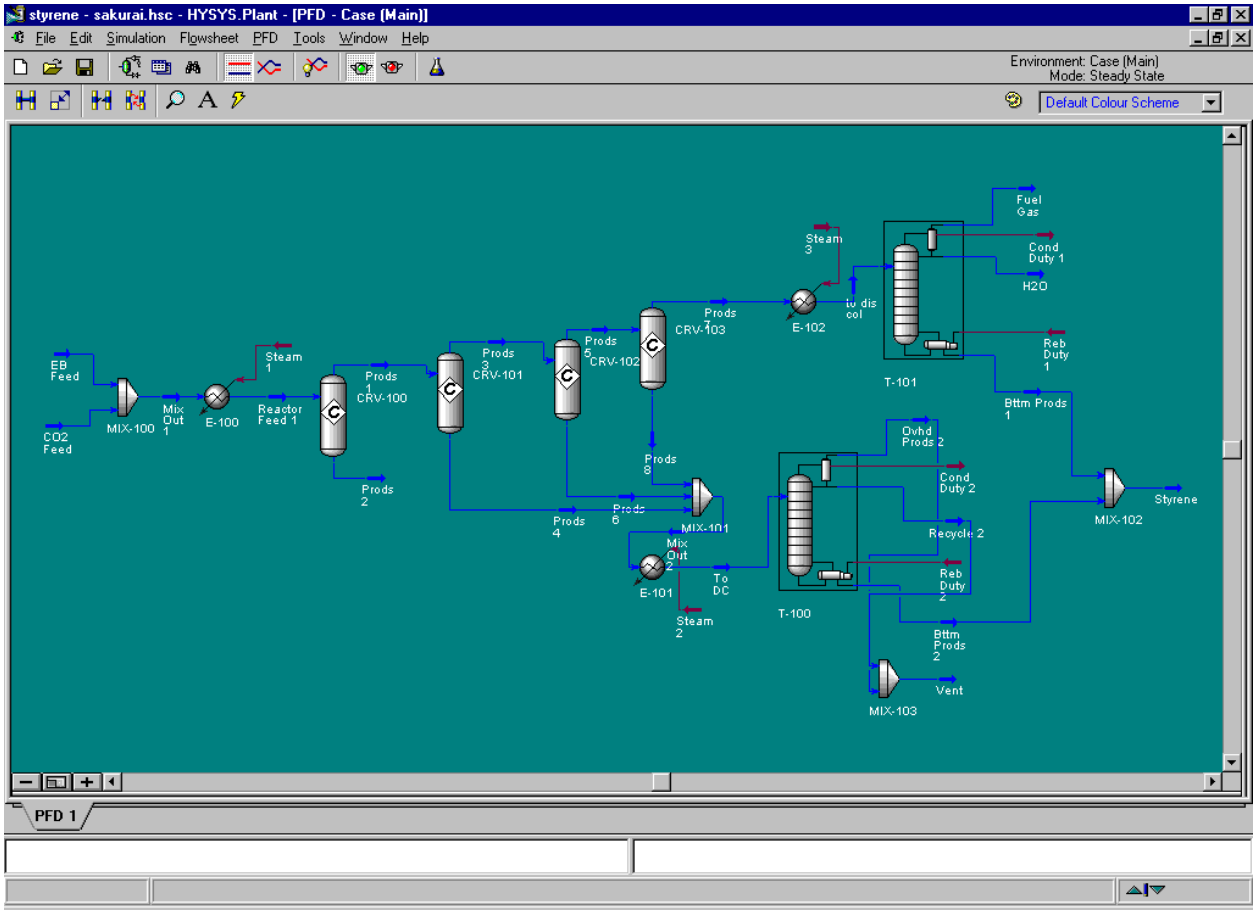


Figure 5. HYSYS Simulation of Styrene Production Process

was estimated to be 1755 kJ/kg-styrene. This potentially new process was included in the chemical complex.

Methanol Synthesis: Toyir, et al., 1998, described methanol synthesis from CO_2 hydrogenation. Raney Cu-Zr catalyst leached with aqueous solution of zincate (NaOH + ZnO) was 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. 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:

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

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

The raw material H_2 is expensive, and this study is combined with another study described by Nishiguchi, et al., 1998. In this research, graphite carbon was produced 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.

$2CH_4 \div 2C + 4H_2$) $H^o = 150$ kJ/mol,) $G^o = 101$ kJ/mol

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

The by-product hydrogen obtained in this study can be used as a raw material for the production of methanol. Thus, the decomposition of natural gas to graphitic carbon and hydrogen described by Nishiguchi, et al., 1998 was combined with the production of methanol by CO_2 hydrogenation described by Toyir, et al., 1998.

The HYSYS flow sheet for this potentially new process is shown in Figure 6. The value added economic model gave a profit of 8.6 cents per pound of methanol for a 47,000 pound per hour plant. The energy required for this process was estimated to be 4335 kJ/kg methanol. This potentially new process was included in the Chemical Complex and Cogeneration Analysis System.

Dehydrogenation of Propane: A process for the production of propylene from dehydrogenation of propane was evaluated. 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 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. The 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. The use of steam cracking (conventional process) to produce the same amount of propylene costs three to four times as much as Oleflex. 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 according to the following reaction.

$C_3H_8 \div C_3H_6 + H_2$) $H^o = 124$ kJ/mol,) $G^o = 86$ kJ/mol.

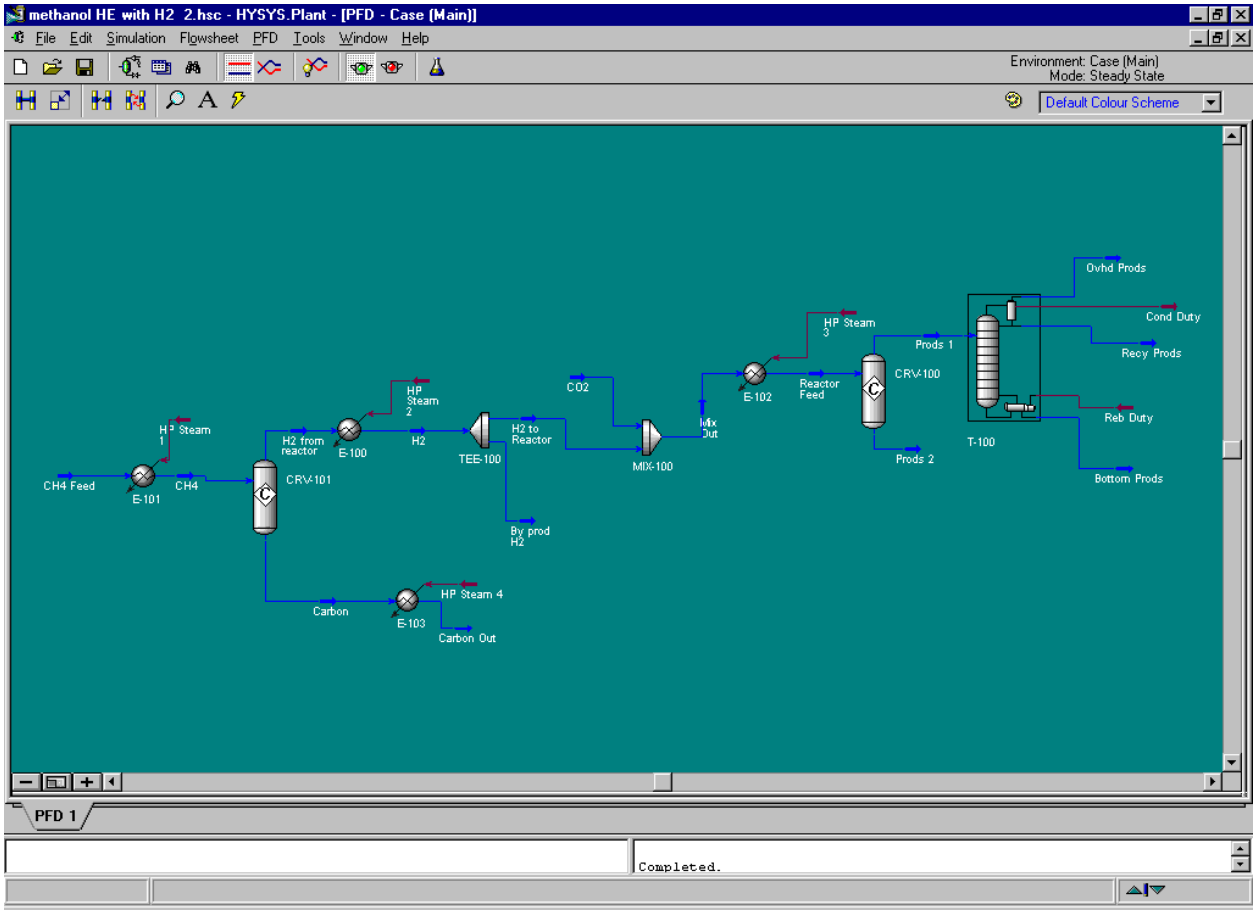
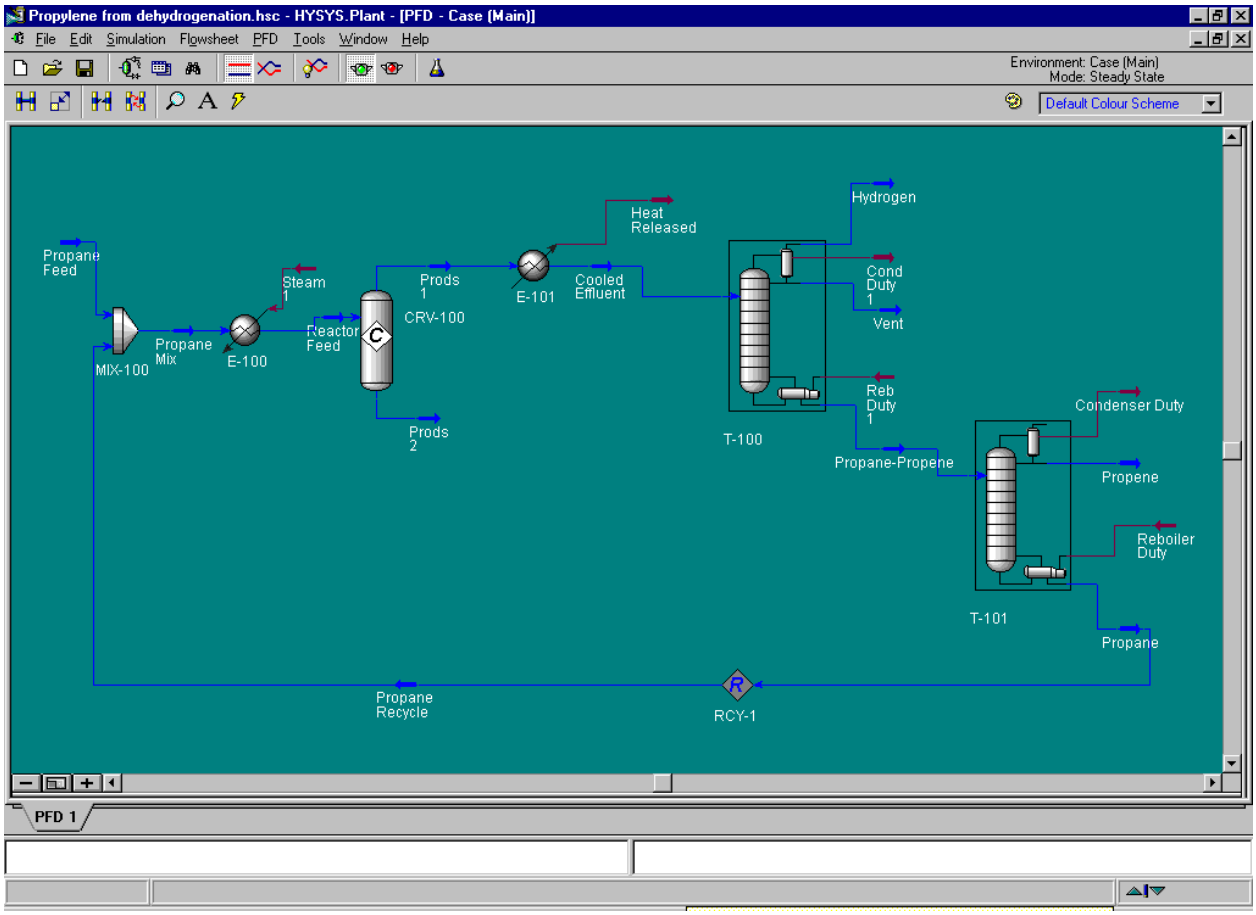


Figure 6. HYSYS Simulation of Methanol Production Process.

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. Unconverted propane, which is in excess of 60% of the feed, is recycled. The catalyst is regenerated (C & EN, June 2003, p.15).

Figure 7. HYSYS Simulation of Propylene Production from Dehydrogenation



Though this process does not use carbon dioxide, it produces hydrogen as a by-product. Thus, this process is simulated using HYSYS. The flow diagram is shown in Figure 7. The energy required for this process was estimated to be 2295 kJ/kg propene. This process is not integrated into the super structure at the present time, but will be incorporated in future to provide a new source of hydrogen for carbon dioxide hydrogenation.

Chemical Complex and Cogeneration Analysis System

The Chemical Complex and Cogeneration Analysis System is being developed by industry-university collaboration for use by corporate engineering groups for regional economic, energy, environmental and sustainable development planning to design energy efficient and environmentally acceptable plants and new products from greenhouse gases. With this System energy, economic and environmental solutions can be developed by process engineers in depth significantly beyond their current capability. System is built on results from previous research on energy efficience and

pollution prevention using on-line optimization, pinch analysis, chemical reactor analysis, pollution assessment and process simulation.

The structure of the System is shown in Figure 8, and the System output includes evaluating the optimum configuration of plants in a chemical production complex based the AIChE Total Cost Assessment(TCA) for economic, energy, environmental and sustainable costs and an integrated cogeneration sequential layer analysis. The input includes incorporating new plants that use greenhouse gases as raw materials in the existing complex of plants.

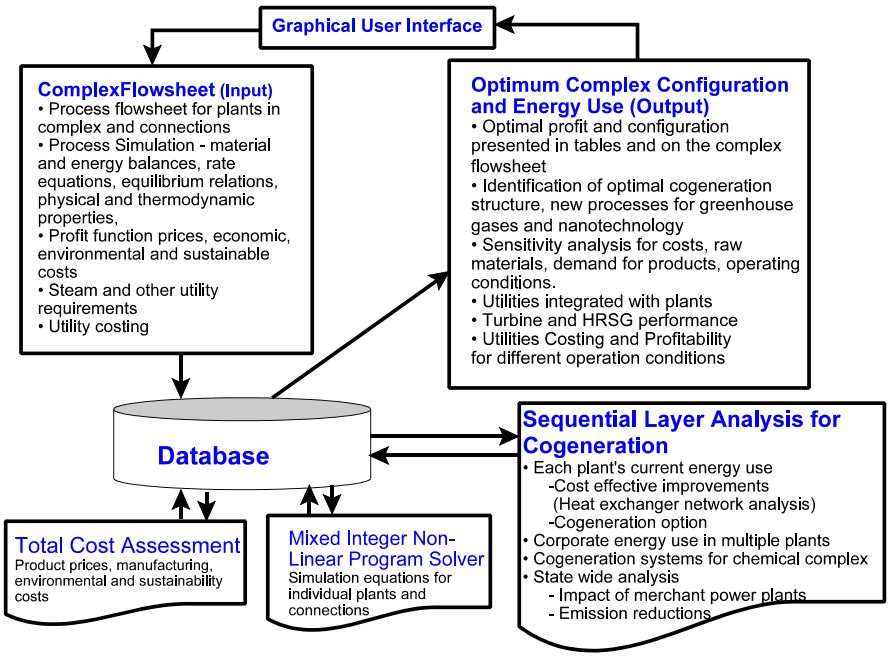


Figure 8 Structure of the Chemical Complex and Cogeneration Analysis System

The AIChE TCA uses five types of costs shown here. There is a detailed spreadsheet with the report that itemizes the components of these costs. The five types of costs from the AIChE TCA have been combined into economic, Types I and II, environmental, Types III and IV, and sustainable, Type V. Sustainable costs are costs to society from damage to the environment by emissions within environmental regulations. For a contact plant for sulfuric acid, emissions are permitted at 4.0 pounds per ton of sulfuric acid produced. Typical sulfuric acid plants have capacities of 3,000 – 4,000 tons per day, and there are about 50 in the Gulf Coast region. Economic costs are estimated by standard methods. Environmental costs are estimated from information given in the AIChE TCA report as a percentage of raw material costs. Sustainable costs are estimated from information given in the AIChE TCA report and other sources such as emission trading costs.

Application of the Chemical Complex and Cogeneration Analysis System

Results using the Chemical Complex Analysis System have demonstrate how new processes using greenhouse gases as raw materials can be integrated into existing chemical complexes. These

processes reduce greenhouse gas emissions and convert them into useful products. For example, the Chemical Complex Analysis System has been applied to an agricultural chemical production complex in the lower Mississippi river corridor. (Hertwig, et al., 2002). Here, ammonia plants produce 0.74 million tons per year of carbon dioxide, and methanol and urea plants consume 0.10 million metric tons per year of carbon dioxide. This leaves a surplus of 0.64 million tons per year of high quality carbon dioxide that can be used in other processes rather than being exhausted to the atmosphere. Preliminary results using the System showed that 0.19 million tons per year of this carbon dioxide could be economically converted to acetic acid, methanol, styrene and propylene, all of which are new, experimental processes and currently not commercialized, as described below.

The base case of existing plants in the chemical production complex is in Figure 9, and there are ten production units plus associated utilities for power, steam and cooling water and facilities for waste treatment. A production unit contains more than one plant; and, for example, the sulfuric acid production unit contains five plants owned by two companies.

For this base case there were 320 equality constraint equations describing the material and energy balances and chemical conversions in the chemical production complex. Also, there were 18 inequality constraint equations describing the demand for product, availability of raw materials and range on the capacities of the individual plants in the complex. The complete model of the complex is available in the Chemical Complex Analysis System program and users manual available from the LSU Mineral Processing Research Institute's web site, http://www.mpri.lsu.edu (Xu et al., 2003).

The raw materials used in the chemical production complex include air, water, natural gas, sulfur, phosphate rock and potassium chloride as shown on Figure 9. The products are a typical granular triple super phosphate (GTSP) [0% N-46% P2O5-0% K2O], mono- and di-ammonium phosphate (MAP [11-52-0] and DAP [18-46-0]), urea [46-0-0], ammonium nitrate [34-0-0], and urea ammonium nitrate solution (UAN) [~30-0-0], phosphoric acid, ammonia and methanol. The flow rates shown on the diagram are in million tons (ton means metric ton) per year. Intermediates are sulfuric acid, phosphoric acid, ammonia, nitric acid, urea and carbon dioxide. The intermediates are used to produce GTSP, MAP and DAP, urea, ammonium nitrate, and UAN. These compounds are either used to make blends or sold directly, but only direct sale are considered in the complex shown in Figure 9. Ammonia, MAP, DAP, UAN and GTSP are used in direct application to crops and other uses. Phosphoric acid can be used in other industrial applications. Methanol is used to produce formaldehyde, methyl esters, amines and solvents, among others, and is included for its use of ammonia plant byproduct - carbon dioxide.

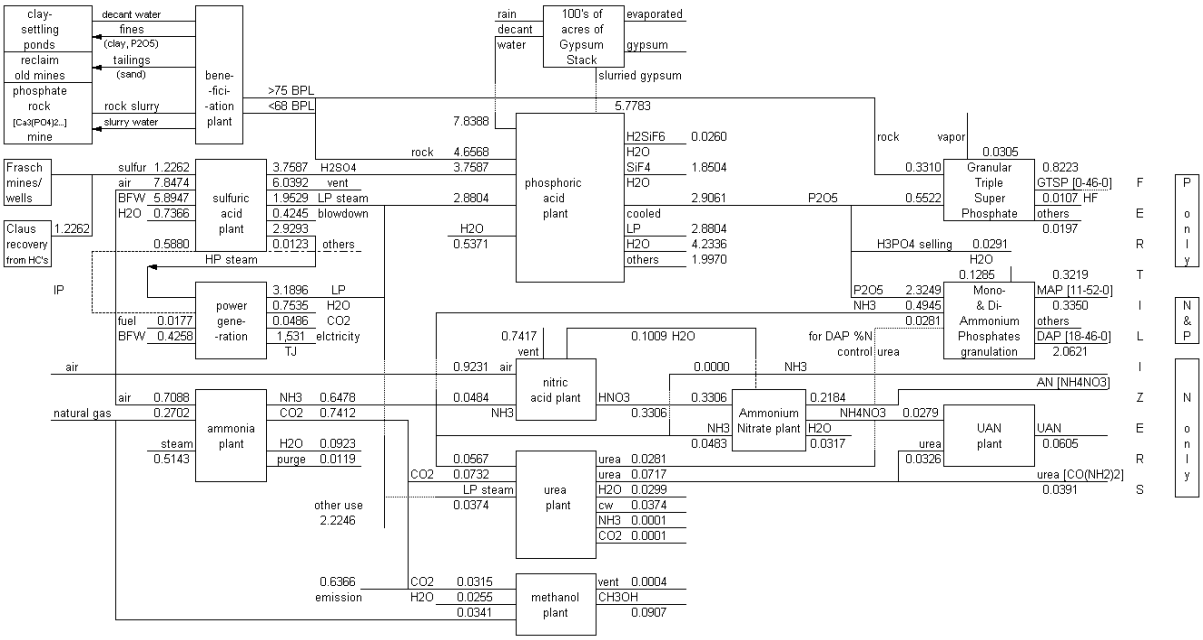


Figure 9 Chemical Production Complex Based on Plants in the Lower Mississippi River Corridor, Base Case. Flow Rates Million TPY

The chemical production complex shown in Figure 9 was expanded into superstructure 1 (Table 4 and Figure 10). Several approaches were incorporated in this expanded complex with alternative ways to produce intermediates that reduce wastes and energy and consume greenhouse gases. 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. The other reacts calcium phosphate ore with HCl to produce phosphoric acid. An ammonium sulfate plant was included to provide an additional blending component. Two gypsum used as a feedstock plants were included to reuse the gypsum waste, one would reduce gypsum to sulfur dioxide which was recycled to sulfuric acid plant; the other would reduced gypsum to sulfur and sulfur dioxide, which were also recycled to sulfuric acid plant. Two acetic acid plants were included compared with base case, one would use the standard commercial method consuming carbon dioxide and methane; the other would use a new and experimental technology for the catalytic reaction of carbon dioxide and methane, also consuming two greenhouse gases. One new catalytic methanol production from methane and carbon dioxide with by-product of hydrogen. One styrene plant uses ethylbenzene and carbon dioxide as feedstocks with by-product of carbon monoxide as fuel. Also, propylene production from dehydrogenation of propane using carbon dioxide is included in the complex. Carbon dioxide,

beyond amounts required in the commercial methanol plant, was used to produce acetic acid, styrene and propylene, the new products for the complex in addition to the new methanol plant.

In summary, the superstructure included three options for producing phosphoric acid, one option for sulfuric acid, and new plants to produce ammonium sulfate, acetic acid, methanol, styrene and propylene, and to recover sulfur and sulfur dioxide. The block flow diagram and associated equations for the superstructure are given by Xu et al. (2001) in the program and users manual. The superstructure had 662 continuous variables, 4 integer variables, 565 equality constraint equations for material and energy balances and 27 inequality constraints for availability of raw materials, demand for product and capacities of the plants in the complex.

Superstructure 2 is a subset of superstructure 1, which did not include the ammonium sulfate plant (Table 5 and Figure 11). This superstructure had 647 continuous variables, 4 integer variables, 554 equality constraint equations for material and energy balances and 26 inequality constraints for availability of raw materials, demand for product and capacities of the plants in the complex.

For base case and superstructure 1 and 2, 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 assumes other manufacturing costs are constant. The sales prices for products and costs of raw materials are given in Table 6. Environmental costs were estimated as 67% of the raw material costs, which is based on the data provided by Amoco, DuPont and Novartis in the AIChE/CRWRT report (Constable et al., 2000). This report lists environmental costs as approximately 20% of the total manufacturing costs and raw material costs as approximately 30% of total manufacturing costs. Sustainable costs were estimated from results given for power generation in the AIChE/CWRT report where carbon dioxide emissions had a sustainable cost of U.S.$3.25 per ton of carbon dioxide. A cost of U.S.$3.25 per ton was charged as a cost to plants that emit carbon dioxide, and plants that consume carbon dioxide were given a credit of twice this cost or U.S.$6.50 per ton. 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 carbon dioxide.

Table 4 Processes in Chemical Production Complex Superstructure 1

Processes in Superstructure 1	
Processes in Base Case	Electric furnace process for phosphoric acid HCl process for phosphoric acid Ammonium sulfate SO_2 recovery from gypsum process S & SO_2 recovery from gypsum process Acetic acid - standard method Acetic acid - new method Methanol - new method Styrene Propylene
Ammonia Nitric acid Ammonium nitrate Urea UAN Methanol Granular triple super phosphate MAP & DAP Power generation Contact process for Sulfuric acid Wet process for phosphoric acid	

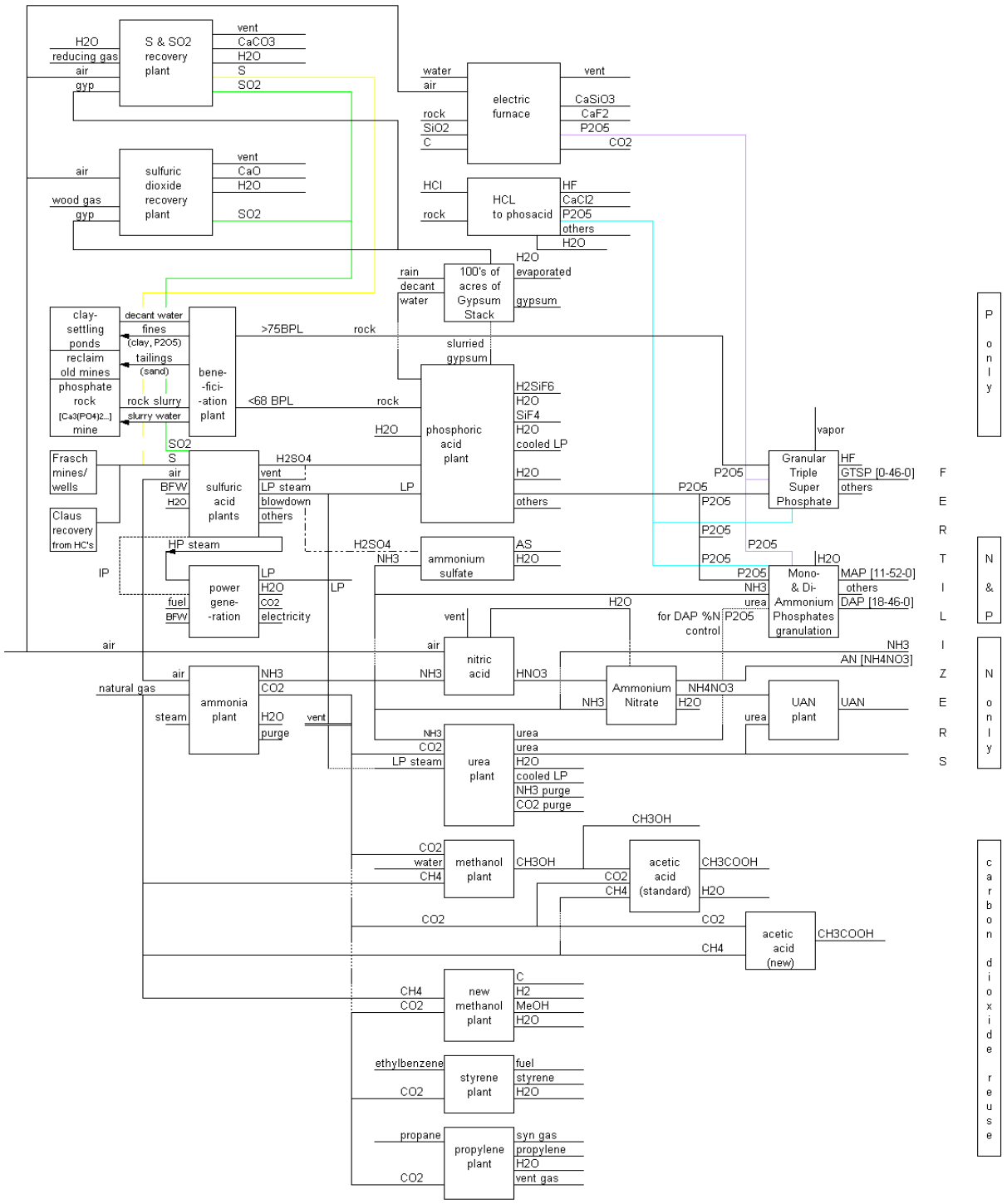


Figure 10 Chemical Production Complex Based on Plants in the Lower Mississippi River Corridor, Superstructure 1.

Table 5 Processes in Agricultural Chemical Complex Superstructure 2

Processes in Superstructure 2	
Processes in Base Case	Electric furnace process for phosphoric acid HCl process for phosphoric acid SO_2 recovery from gypsum process S & SO_2 recovery from gypsum process Acetic acid - standard method Acetic acid - new method Methanol - new method Styrene Propylene
Ammonia Nitric acid Ammonium nitrate Urea UAN Methanol Granular triple super phosphate MAP & DAP Power generation Contact process for Sulfuric acid Wet process for phosphoric acid	

Table 6 Raw Material and Product Prices
Source Green Market Sheet (July 10, 2000), Internet and AIChE/CWTR TCA Report

Raw Materials	Cost ($/T)	Raw Materials	Cost ($/T)	Products	Price($/T)
Natural Gas	245	Market cost		Ammonia	190
Phosphate Rock		for short term		Methanol	96
wet process	27	purchase		Acetic Acid	623
electrofurnace	24	Debit for NOx	1025	GTSP	142
HCl process	25	Production		MAP	180
GTSP process	30	Credit for CO2	6.50	DAP	165
HCl	50	Consumption		NH4NO3	153
Sulfur		Debit for CO2	3.25	UAN	112
Frasch	42	Production		Urea	154
Claus	38	Credit for HP Steam	10	Graphite	760
Ethylbenzene	551	Credit for IP Steam	6.4	Hydrogen	3528
Propane	180	Credit for gypsum	5	CO	45
Reducing gas	1394	Consumption		Styrene	661
Wood gas	634	Debit for gypsum	2.5	Propylene	374
C electrofurnace	760	Production		Syngas	316

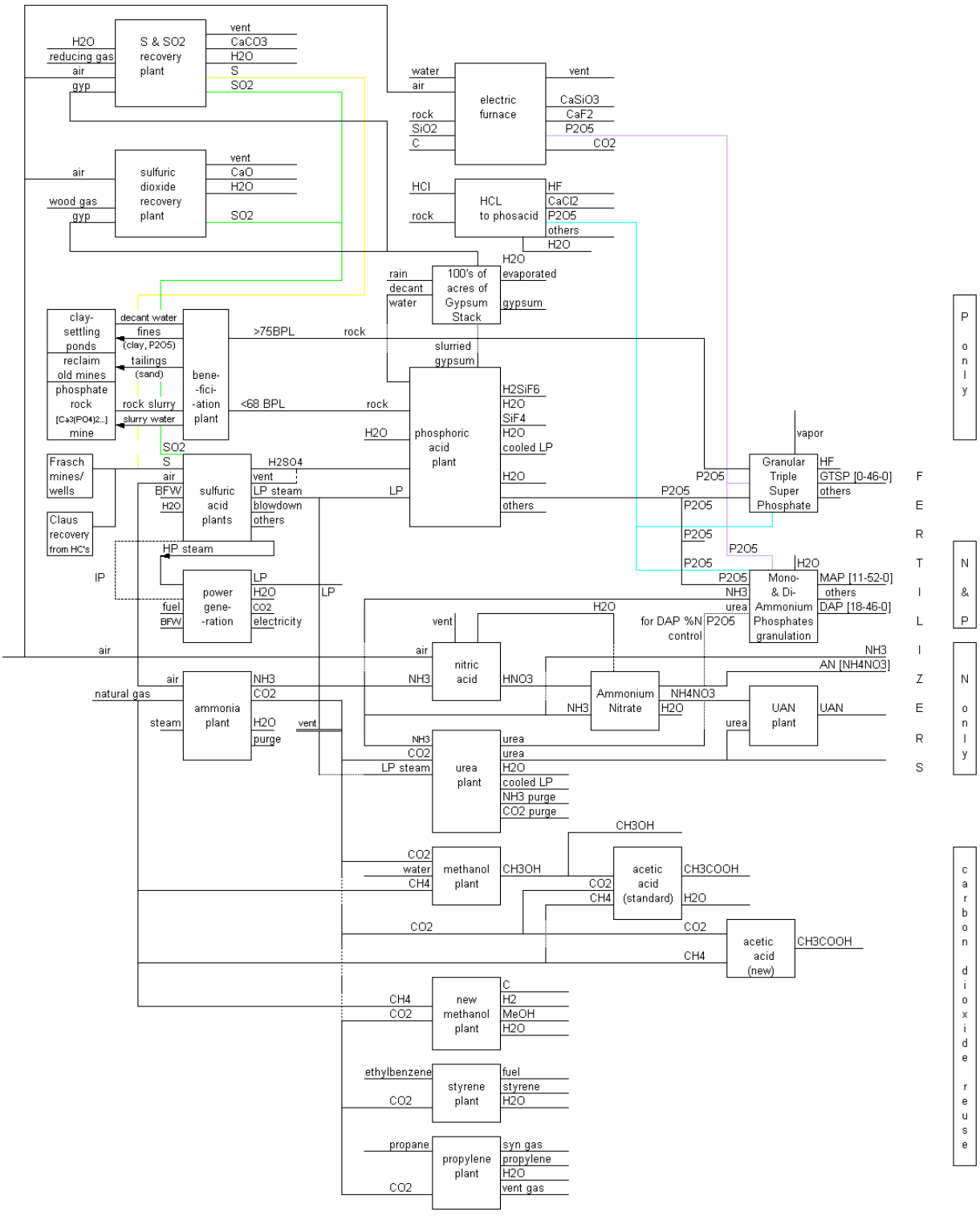


Figure 11 Chemical Production Complex based on Plants in the Lower Mississippi River Corridor, Superstructure 2

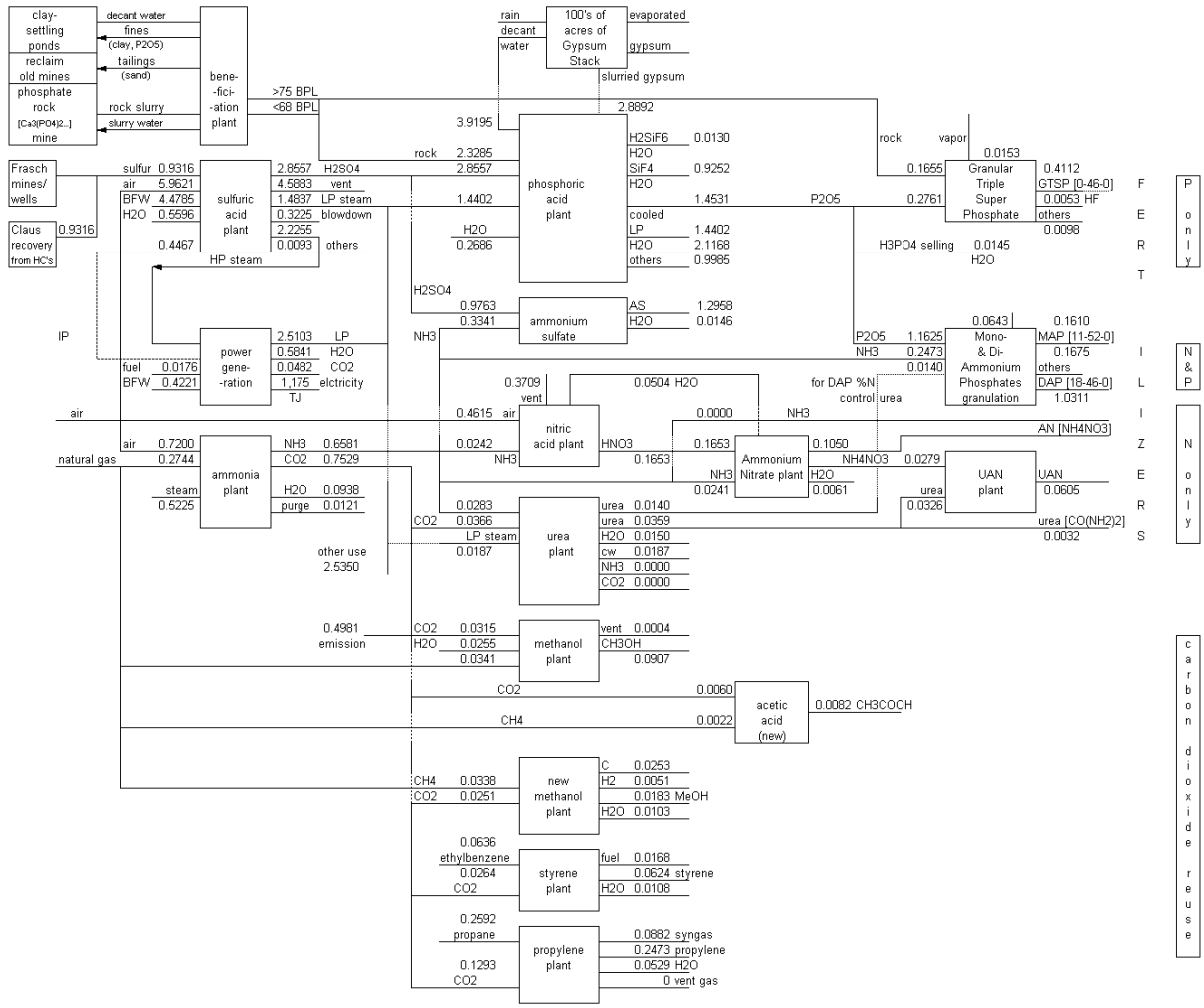


Figure 12 Chemical Production Complex Based on Plants in the Lower Mississippi River Corridor, Optimal Structure 1 from Superstructure 1. Flow Rates Million TPY

The System was used to obtain the optimum configuration of plants from the superstructure. The complete solution is given by Xu et al. (2003), and a comparison of the base case and the optimal solution from the superstructure 1 is summarized in Table 7, Figure 12 and Figure 13. The optimal solution from superstructure 2 is in Table 8, Figure 13 and Figure 14.

For optimal solution 1, the profit increased about 109% from the base case to the optimal solution 1. Also, as shown in the Table 7, environmental cost decreased about 9.9%, and sustainable costs increased about 0.36% because of the increased CO2 emission from power plant outweighing the credit from CO2 reuse as feedstock. Production rates for the products in the optimal solution were constrained by their capacity limit, which were set at the base case values. In addition, the acetic acid plant where acetic acid is produced from carbon dioxide and methane direct reaction was operating at the upper limit instead of the standard commercial plant, and it was optimal to operate the ammonium sulfate plant. Meanwhile, the energy requirement of ammonium nitrate plant was different from base and optimal solution 1 based on the same production rate because the different production rate of two types of ammonium nitrate which are ammonium nitrate solution and granular ammonium nitrate. The ammonia plant in the optimal solution 1 ran at the full capacity to provide ammonia mostly to ammonium sulfate plant which is very profitable. Since ammonium sulfate consumed a significant amount of ammonia which caused the production rates of other products in the complex decreased.

For optimal solution 2, the profit increased about 49% from the base case to the optimal solution 2. Also, as shown in the Table 8, environmental cost increased about 217%, and sustainable costs decreased about 9.4% because the CO2 reuse in the new plants outweighed the increased CO2 emission from power plant. All the production plants in the base case kept running at the same production rates in the optimal solution as in the base case. The only difference is the additional new plants were incorporated to maximize the complex profit, i.e., new acetic acid, new methanol, styrene and propylene plant which used CO2 as feedstock to decrease the sustainable costs of the complex.

These results illustrated the capability of the system to select an optimum configuration of plants in a chemical production complex and incorporate economic, environmental and sustainable costs.

		Base case		Optimal structure	
Profit (U.S.$/year)		157,110,506		327,778,661	
Environmental cost (U.S.$/year)		174,102,300		156,853,000	
Sustainable cost (U.S.$/year)		-18,025,600	energy	-17,960,800	energy
Plant name	Capacity (t/year)	Capacity	requirement	Capacity	requirement
	(upper-lower bounds)	(t/year)	(TJ/year)	(t/year)	(TJ/year)
Ammonia	329,030-658,061	647,834	3,774	658,061	3,820
Nitric acid	0-178,547	178,525	-649	89,262	-324
Ammonium nitrate	113,398-226,796	226,796	116	113,398	27
Urea	49,895-99,790	99,790	127	49,895	64
Methanol	90,718-181,437	90,719	1,083	90,719	1,083
UAN	30,240-60,480	60,480	0	60,480	0
MAP	0-321,920	321,912		160,959	
DAP	0-2,062,100	2,062,100	2,127	1,031,071	1,069
GTSP	0-822,300	822,284	1,036	411,150	518
Contact process sulfuric acid	1,851,186-3,702,372	3,702,297	-14,963	2,812,817	-11,368
Wet process phosphoric acid	697,489-1,394,978	1,394,950	7,404	697,489	3,702
Electric furnace phosphoric acid	0-1,394,978	na	na	0	0
HCl to phosphoric acid	0-1,394,978	na	na	0	0
Ammonium sulfate	0-2,839,000	na	na	1,295,770	733
Acetic acid (standard)	0-8,165	na	na	0	0
Acetic acid (new)	0-8,165	na	na	8,165	92
SO2 recovery from gypsum	0-1,804,417	na	na	0	0
S & SO2 recovery from gypsum	0-903,053	na	na	0	0
Methanol (new)	9,144-18,288	na	na	18,288	82
H2 from methanol (new)	0-5,050	na	na	5,050	
Styrene	62,396-124,791	na	na	62,396	66
Propylene	123,647-247,294	na	na	247,294	718
Ammonia sale		0		0	
Ammnium Nitrate sale		218,441		105,043	
Urea sale		39,076		3,223	
Wet process phosphoric acid sale		13,950		6,975	
Total energy requirement			55		282

Table 8 Comparison of Base Case and Optimal Structure 1

		Base case		Optimal structure	
Profit (U.S.$/year)		157,110,506		233,671,605	
Environmental cost (U.S.$/year)		174,102,300		211,303,300	
Sustainable cost (U.S.$/year)		-18,025,600	energy	-19,713,300	energy
Plant name	Capacity (t/year)	Capacity	requirement	Capacity	requirement
	(upper-lower bounds)	(t/year)	(TJ/year)	(t/year)	(TJ/year)
Ammonia	329,030-658,061	647,834	3,774	647,834	3,774
Nitric acid	0-178,547	178,525	-649	178,525	-649
Ammonium nitrate	113,398-226,796	226,796	116	226,796	116
Urea	49,895-99,790	99,790	127	99,790	127
Methanol	90,718-181,437	90,719	1,083	90,719	1,083
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	2,127	2,062,100	2,127
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
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
Acetic acid (standard)	0-8,165	na	na	0	0
Acetic acid (new)	0-8,165	na	na	8,165	92
SO2 recovery from gypsum	0-1,804,417	na	na	0	0
S & SO2 recovery from gypsum	0-903,053	na	na	0	0
Methanol (new)	9,144-18,288	na	na	18,288	82
H2 from methanol (new)	0-5,050	na	na	5,050	
Styrene	62,396-124,791	na	na	62,396	66
Propylene (S914)	123,647-247,294	na	na	247,294	718
Ammonia sale		0		0	
Ammnium Nitrate sale		218,441		218,441	
Urea sale		39,076		39,076	
Wet process phosphoric acid sale		13,950		13,950	
Total energy requirement			55		1,013

Table 9 Comparison of Base Case and Optimal Structure 2

Conclusions

The System has been applied to a chemical production complex with ten multiple plant production units in the lower Mississippi river corridor. The optimal configuration of plants was determined based on economic, environmental and sustainable costs. A comparison of the current configuration of units with the optimal one was made. For superstructure 2, the profit increased about 49% from the base case to the optimal solution 2. Also, environmental cost increased about 21%, and sustainable costs decreased about 9.4%. These results illustrated the capability of the system to select an optimum configuration of plants in an agricultural chemical complex and incorporate economic, environmental and sustainable costs. These results are for several new chemical plants incorporated in the existing production complex and are typical of results that can be expected from applying the Chemical Complex and Cogeneration Analysis System to existing chemical production complexes worldwide.

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Identifying and Developing New, Carbon Dioxide Consuming Processes

Aimin Xu, Sudheer Indala, Thomas A. Hertwig, Ralph W. Pike

F. Carl Knopf, Carl L. Yaws and Jack R. Hopper

A joint industry-university research effort

IMC Phosphates, Motiva Enterprises,

Louisiana State University, Lamar University

2003 AIChE Annual Meeting, Paper 408b, November 16 - 21, 2003

San Francisco, CA

Overview of Presentation

- Introduction
- Related work and programs
- Chemical Complex and Cogeneration Analysis System
- Greenhouse gases: emissions and utilization
- Identify and design new CO_2 consuming processes
- Results
- Conclusions

Introduction

- Domestic chemical industry
  - Current situation
    - 6.3 quads energy
    - 70,000 diverse products
  - Challenges
    - Inefficient power generation
    - Greenhouse gas emission constraints

Pellegrino, DOE chemical IOF report , 2002

Introduction

- Pollution prevention
  - was an environmental issue
  - now a critical business opportunity
- Long term cost of ownership must be evaluated with short term cash flows.
- Companies undergoing difficult institutional transformations
- Emphasis on pollution prevention has broadened to include:
  - Total (full) cost accounting
  - Life cycle assessment
  - Sustainable development
  - Eco-efficiency (*eco*nomic and *eco*logical)

Introduction

- Opportunities
  - Processes for conversion of greenhouse gases to valuable products
  - Cogeneration
- Methodology
  - Chemical Complex and Cogeneration Analysis System
  - Application to chemical complex in the lower Mississippi River corridor

Related Work and Programs

- Aspen Technology
- Department of Energy (DOE)
  www.oit.doe.gov/bestpractice
- Environmental Protection Agency (EPA)
  www.epa.gov/opptintr/greenengineering

Chemical Complex and Cogeneration Analysis System

Objective: To give corporate engineering groups new capability to design:

- New processes for products from greenhouse gases
- Energy efficient and environmentally acceptable plants

Chemical Complex and Cogeneration Analysis System

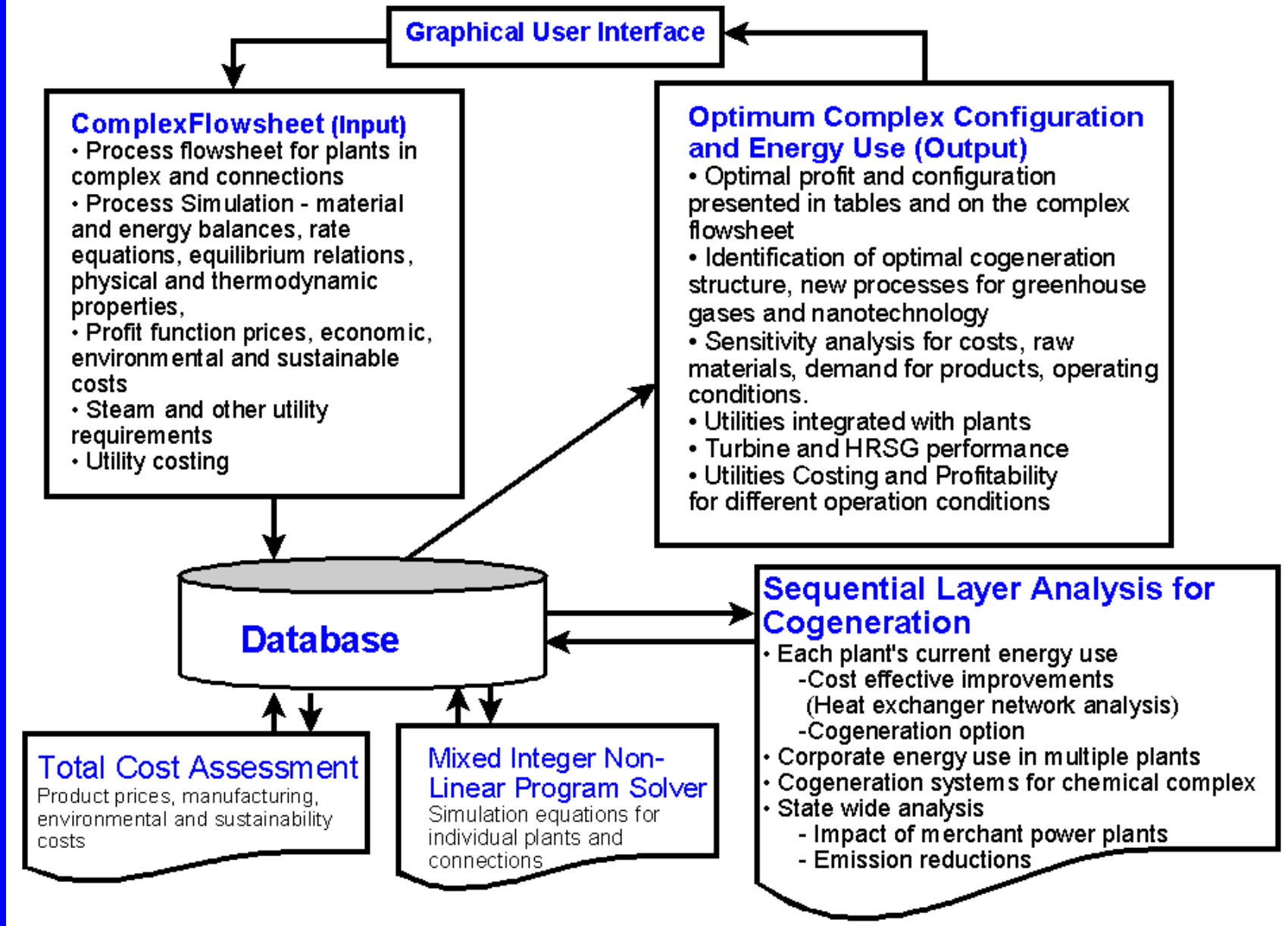
Chemical Complex Analysis System

Determines the best configuration of plants in a chemical complex based on the AIChE Total Cost Assessment (TCA) and incorporates EPA Pollution Index methodology (WAR) algorithm

Cogeneration Analysis System

Determines the best energy use based on economics, energy efficiency, regulatory emissions and environmental impacts from greenhouse gas emissions.

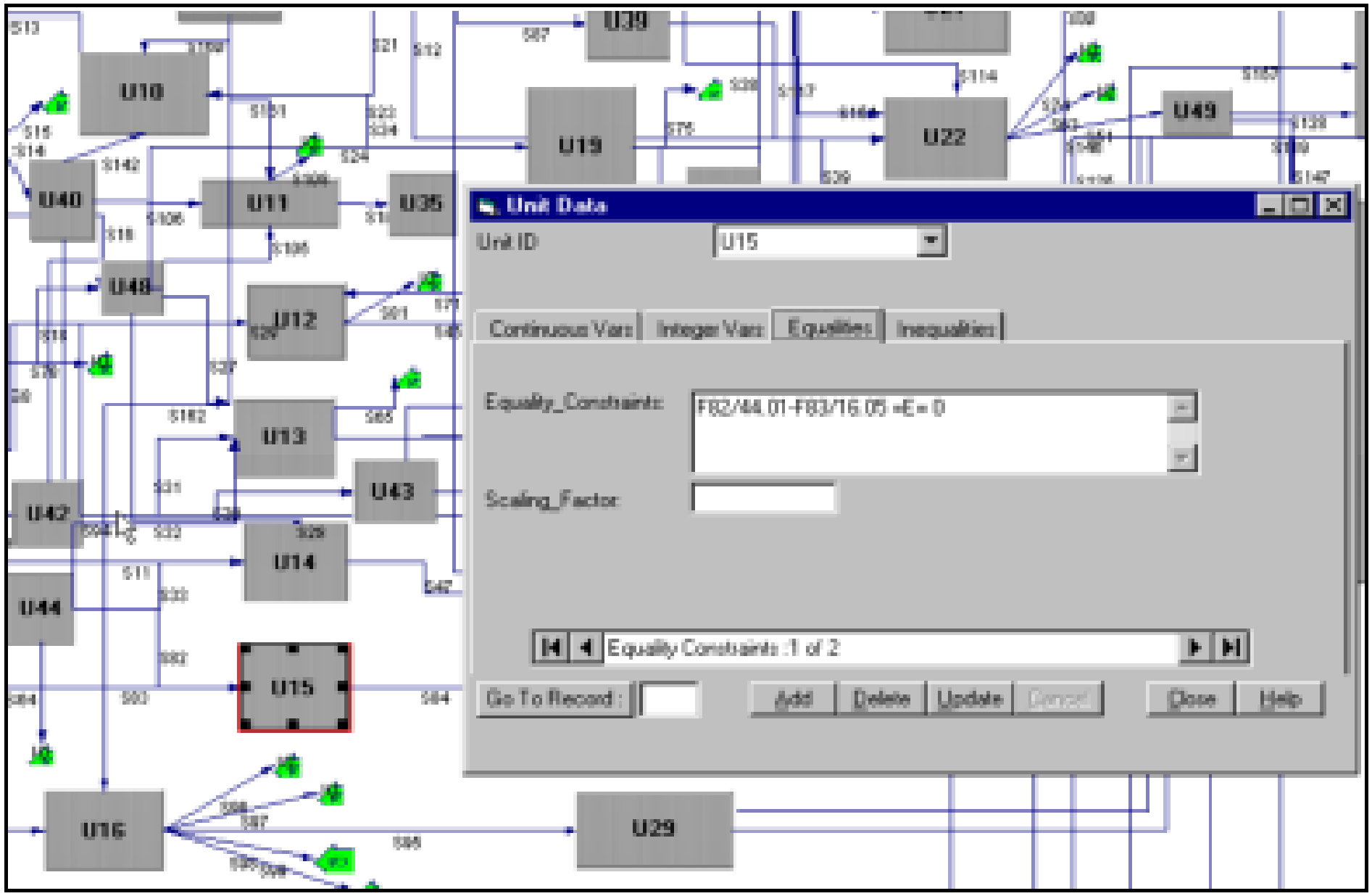
Structure of the System



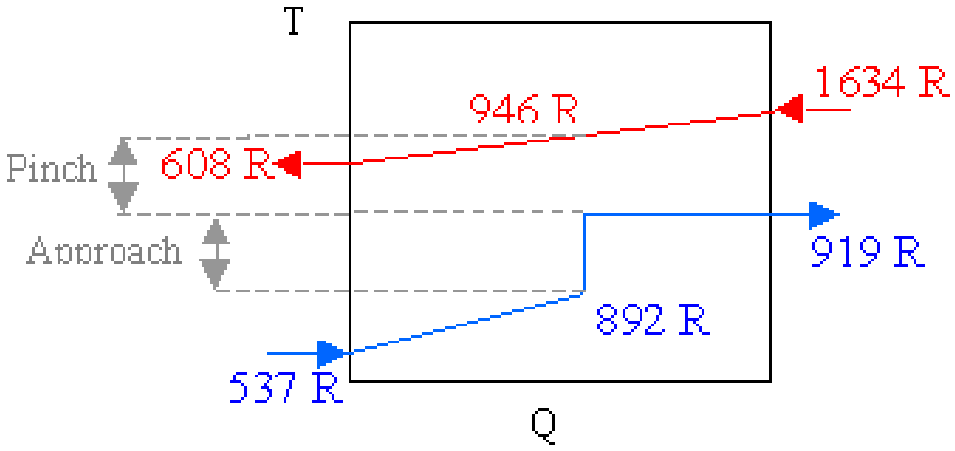
AIChE Total Cost Assessment

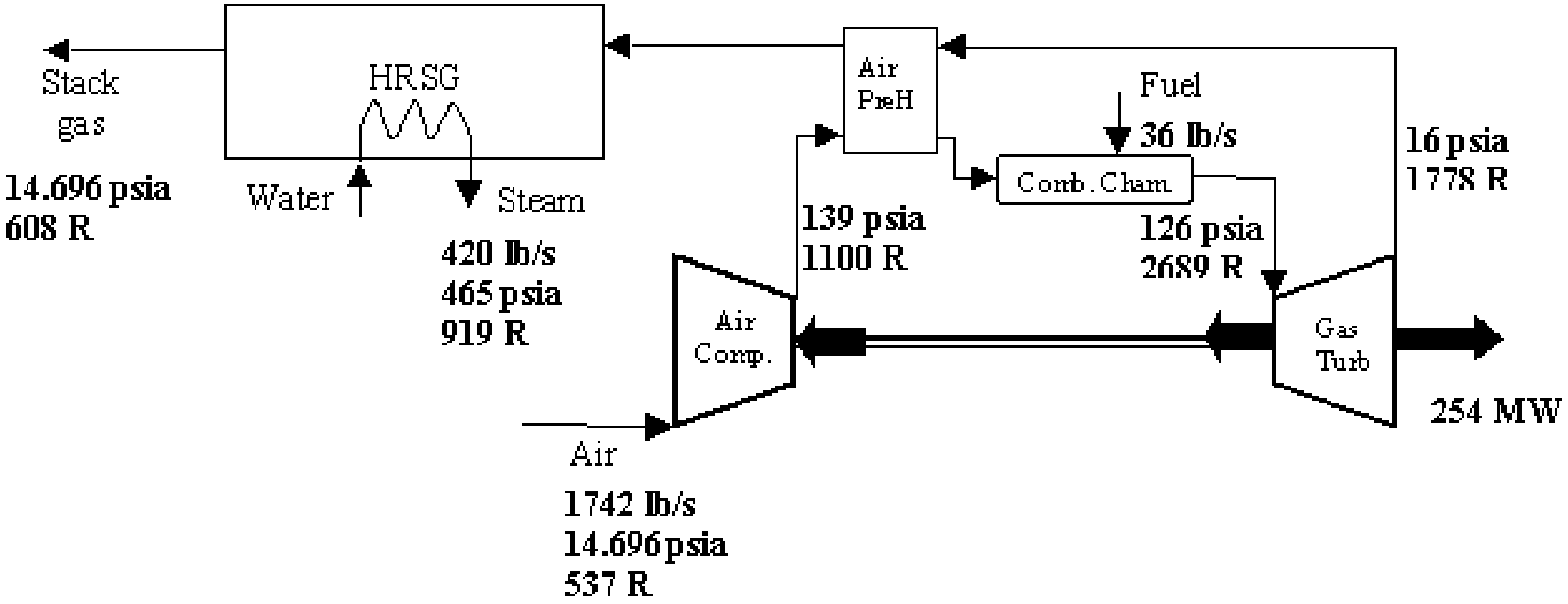
- Includes five types of costs: I direct, II overhead, III liability, IV internal intangible, V external (borne by society - sustainable)
- Sustainable costs are costs to society from damage to the environment caused by emissions within regulations, e.g., sulfur dioxide 4.0 lb per ton of sulfuric acid produced
- Environmental costs: compliance, fines, 20% of manufacturing costs
- Combined five TCA costs into economic, environmental and sustainable costs
  - Economic: raw materials, utilities, etc
  - Environmental: 67% of raw materials
  - Sustainable: estimated from sources

Illustration of Input to the System for Unit Data

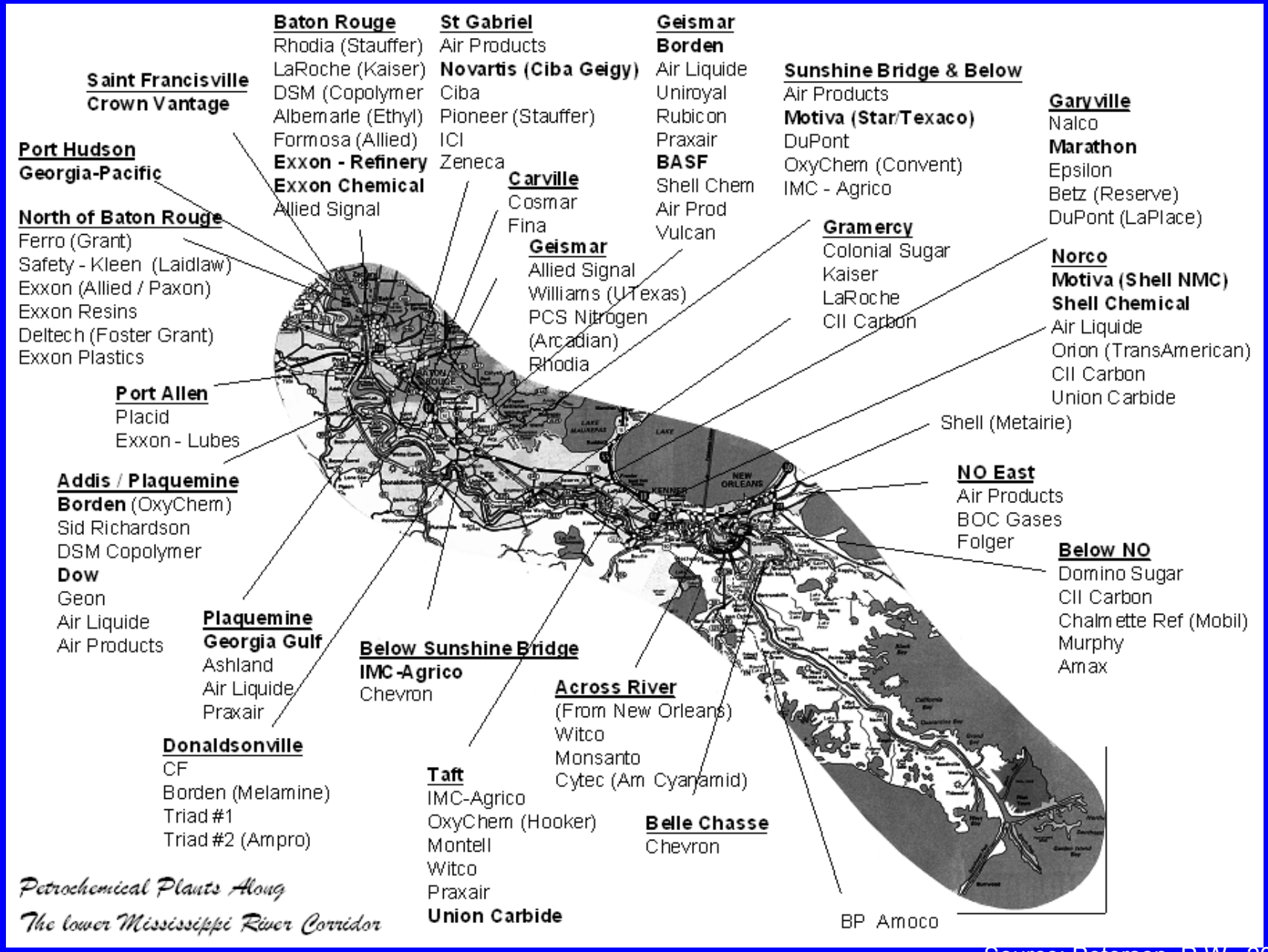


Typical Cogeneration Results on the CHP Diagram



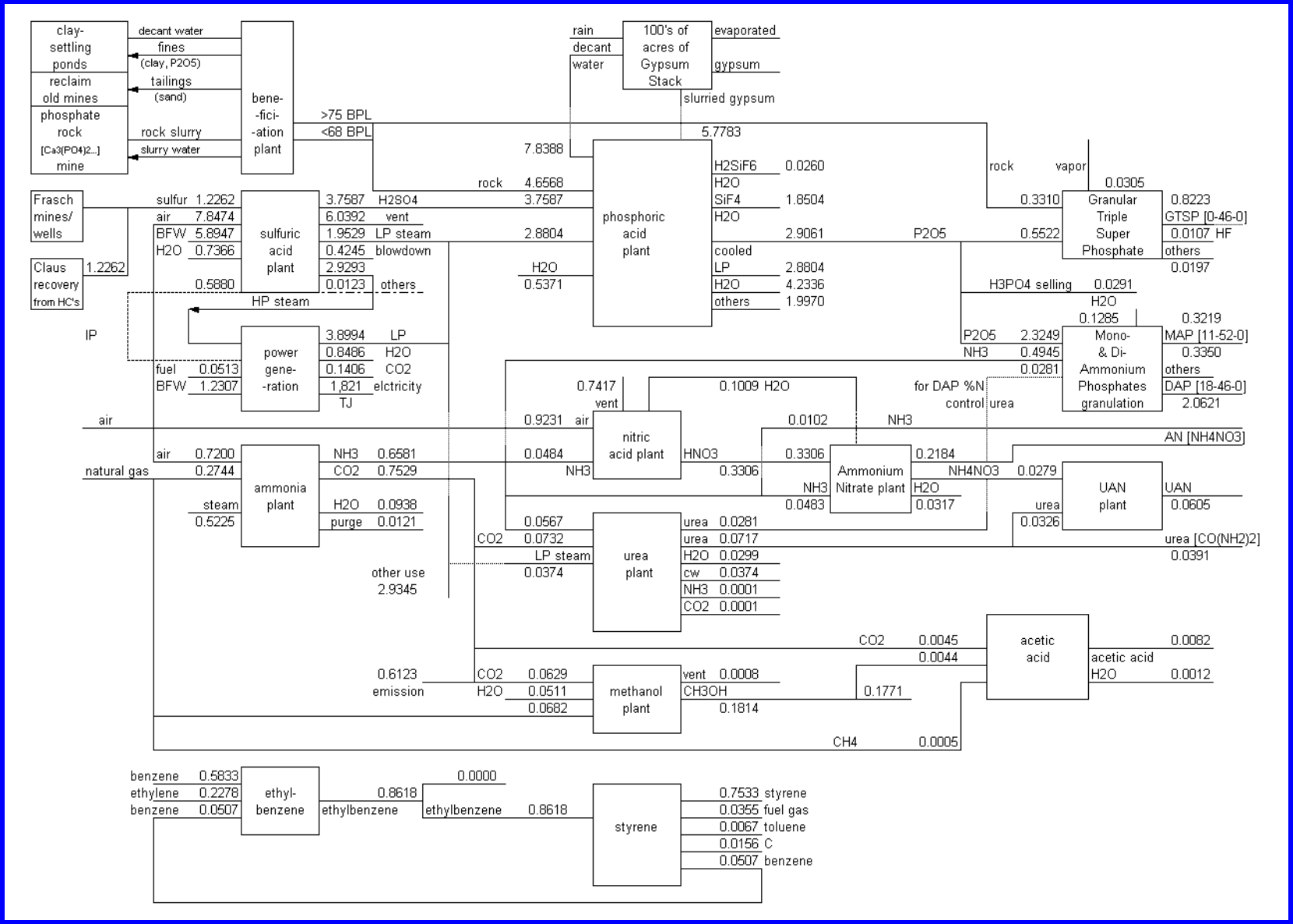


Plants in the lower Mississippi River Corridor



Source: Peterson, R.W., 2000

Chemical Complex



Plants in the lower Mississippi River Corridor, Base Case. Flow Rates in Million Tons Per Year

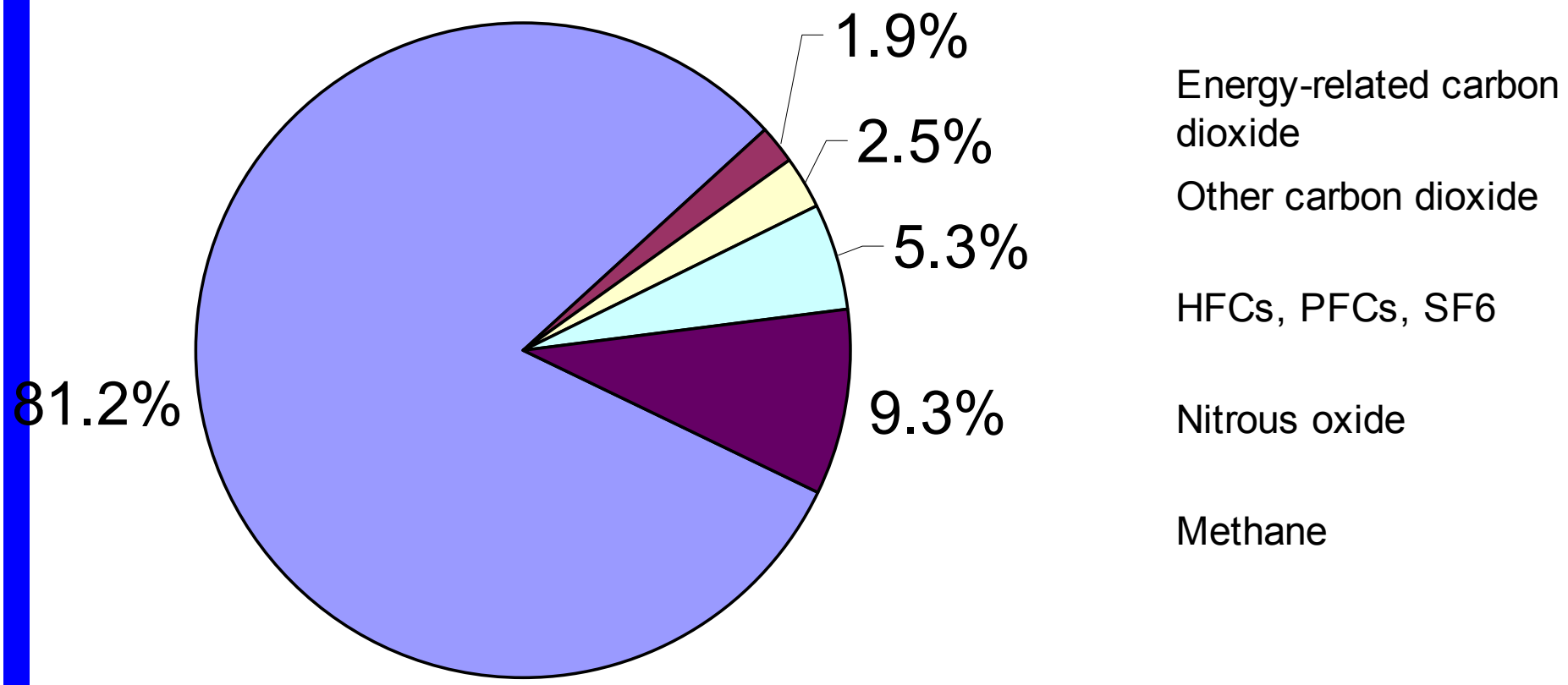
Some Chemical Complexes in the World

- North America
  - Gulf coast petrochemical complex in Houston area (U.S.A.)
  - Chemical complex in the Lower Mississippi River Corridor (U.S.A.)
- South America
  - Petrochemical district of Camacari-Bahia (Brazil)
  - Petrochemical complex in Bahia Blanca (Argentina)
- Europe
  - Antwerp port area (Belgium)
  - BASF in Ludwigshafen (Germany)
- Oceania
  - Petrochemical complex at Altona (Australia)
  - Petrochemical complex at Botany (Australia)

Some Chemical Complexes in the World (Continued)

- Asia
  - The Singapore petrochemical complex in Jurong Island (Singapore)
  - 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)
  - Jamnagar refinery and petrochemical complex (India)
  - Sabic company based in Jubail Industrial City (Saudi Arabia)
  - Petrochemical complex in Yanbu (Saudi Arabia)
  - Equate (Kuwait)
- Africa
  - petrochemical industries complex at Ras El Anouf (Libya)

Greenhouse Gas Emissions



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

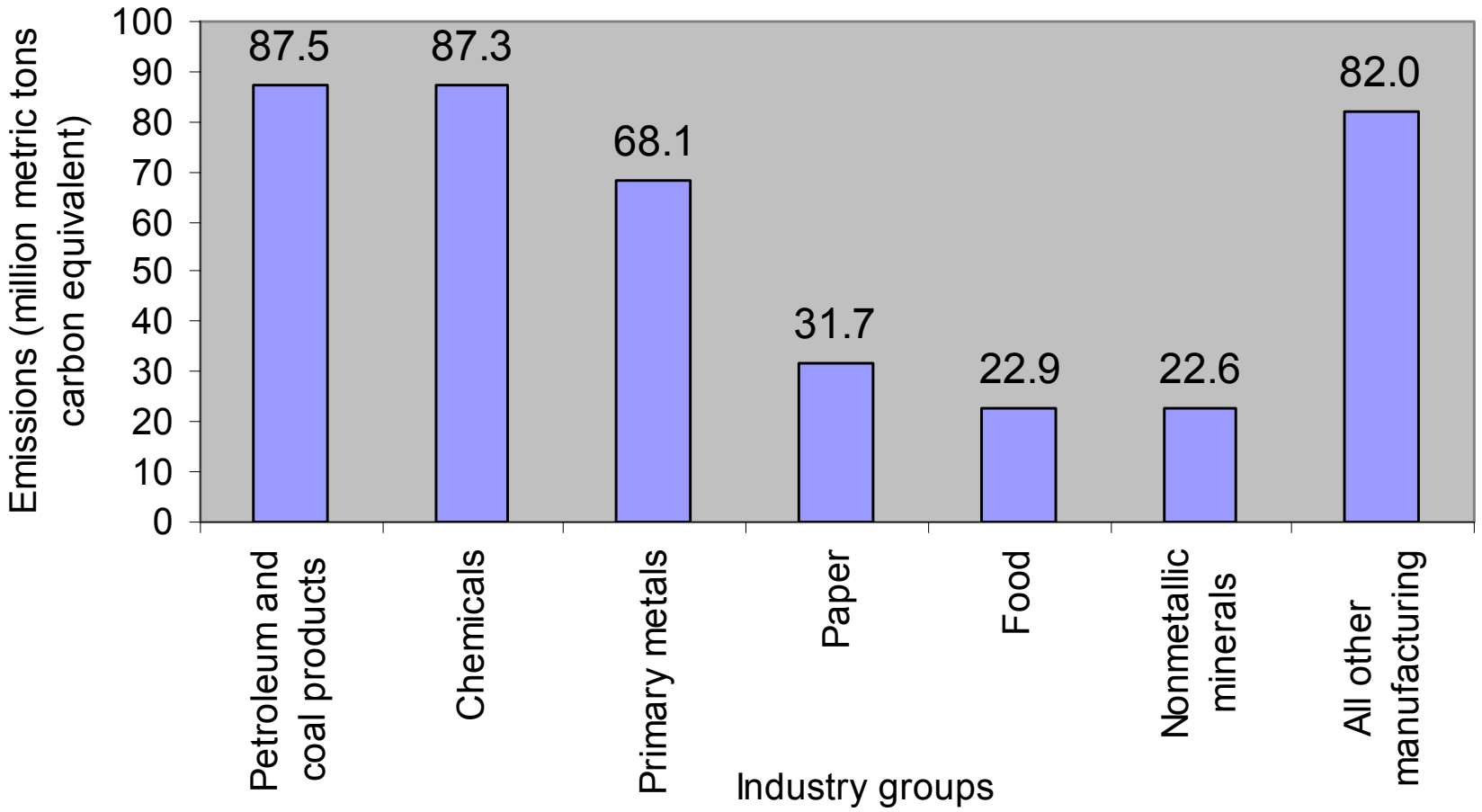
CO_2 Sources and Cycle

From IPCC (1995)

Unit – GT of C per year

- Natural Source
  - – Ocean: 90 (57.29%)
  - – Plants and soil: 60 (38.19%)
- Anthropogenic source
  - – Burning fossil fuels: 5.5 (3.50%)
  - – Deforestation: 1.6 (1.02%)
- Total: 157.1 (100%)

CO_2 Emissions from Industries



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

Carbon Dioxide Emissions

(Million Metric Tons Carbon Equivalent Per Year)

- Total CO_2 added to atmosphere
  - Burning fossil fuels
  - Deforestation
- Total worldwide CO_2 from consumption and flaring of fossil fuels
  - United States 5,500
  - China 1,600
  - Russia 792
  - Japan 1,526
  - All others
- U.S. CO_2 emissions
  - Industry 440
  - Buildings 307
  - Transportation 3,258
  - Total
- U.S. industry (manufacturing): Petroleum, coal products and chemicals 624 175
- Chemical complex in the lower Mississippi River corridor excess high purity CO_2 630 0.61

473

Surplus Carbon Dioxide

- Ammonia plants produce 0.75 million tons per year in lower Mississippi River corridor.
- Methanol and urea plants consume 0.15 million tons per year.
- Surplus high-purity carbon dioxide 0.60 million tons per year vented to atmosphere.
- Plants are connected by CO_2 pipelines.

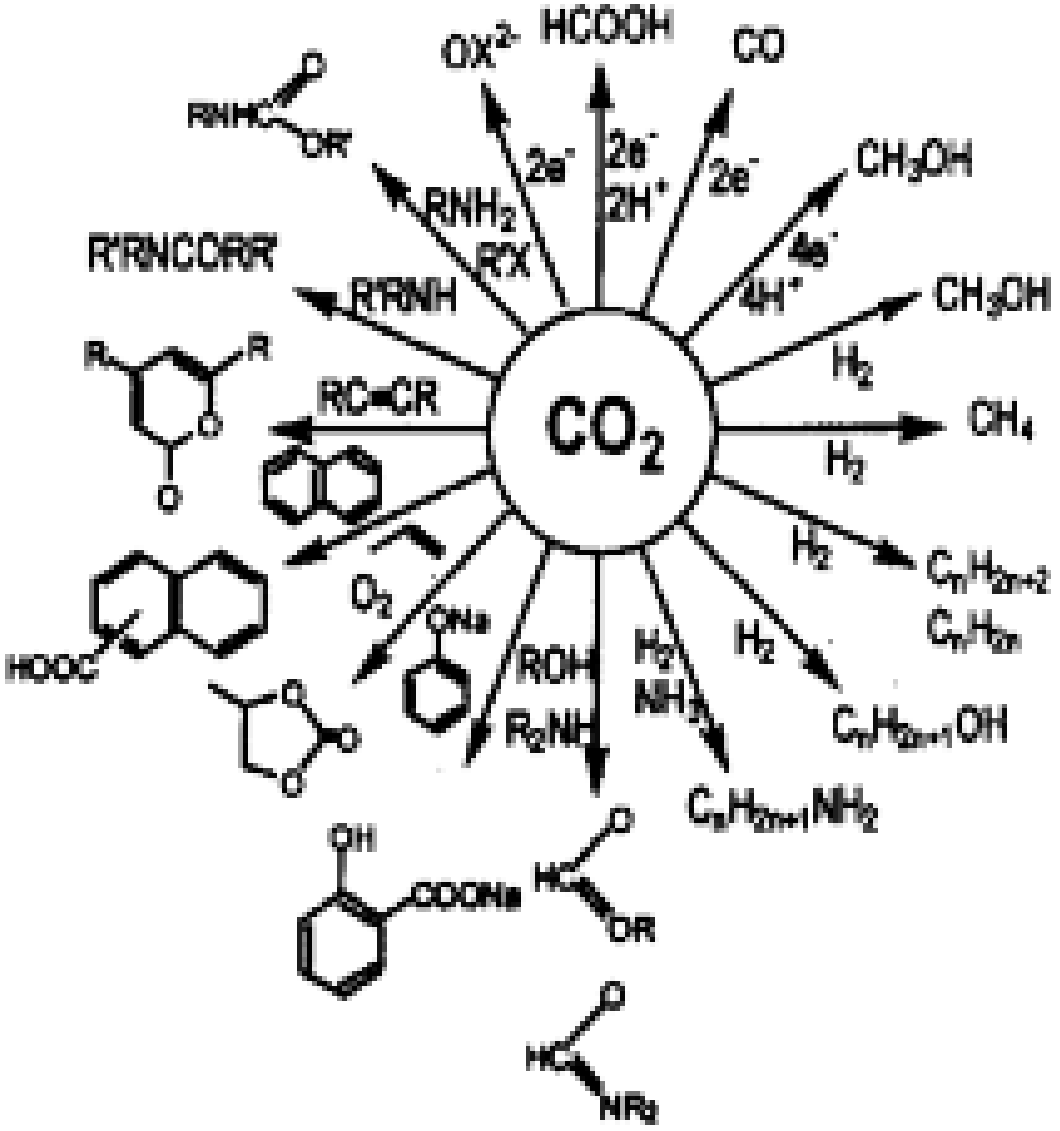
Commercial Uses of CO_2

110 million tons of CO_2 for chemical synthesis

- Urea (chiefly, 90 million ton of CO_2)
- Methanol (1.7 million tons of CO_2)
- Polycarbonates
- Cyclic carbonates
- Salicylic acid
- Metal carbonates

Greenhouse Gases as Raw Material

- Intermediate of fine chemicals for the chemical industry
  -C(O)O-: Acids, esters, lactones
  -O-C(O)O-:Carbonates
  -NC(O)OR-: Carbamic esters
  -NCO: Isocyanates
  -N-C(O)-N: Ureas
- Use as a solvent
- Energy rich products
  CO, CH_3OH



Catalytic Reactions of CO_2

Hydrogenation

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

$2CO_2 + 6H_2 \rightarrow C_2H_5OH + 3H_2O$ ethanol

$CO_2 + H_2 \rightarrow CH_3\text{-}O\text{-}CH_3$ dimethyl ether

Hydrolysis and Photocatalytic Reduction

$CO_2 + 2H_2O \rightarrow CH_3OH + O_2$

$CO_2 + H_2O \rightarrow HC{=}O\text{-}OH + 1/2O_2$

$CO_2 + 2H_2O \rightarrow CH_4 + 2O_2$

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

$CO_2 + H_2 \rightarrow HC{=}O\text{-}OH$ formic acid

$CO_2 + CH_4 \rightarrow CH_3\text{-}C{=}O\text{-}OH$ acetic acid

Other Reactions

CO_2 + ethylbenzene $\rightarrow$styrene

$CO_2 + C_3H_8 \rightarrow C_3H_6 + H_2 + CO$
dehydrogenation of propane

$CO_2 + CH_4 \rightarrow 2CO + H_2$ reforming

Graphite Synthesis

$CO_2 + H_2 \rightarrow C + H_2O$

$CH_4 \rightarrow C + H_2$
$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

Amine Synthesis

$CO_2 + 3H_2 + NH_3 \rightarrow CH_3\text{-}NH_2 + 2H_2O$ methyl amine and higher amines

Methodology of Developing Process Information for the System

- Identifying potentially new processes
- Simulating with HYSYS
- Estimating utilities required
- Evaluating value added economic analysis
- Selecting best processes based on value added economic profit
- Integrating into the superstructure

Identifying Potentially New Processes

- Literature review of new experimental studies
- Comparing with the existing commercial processes
- Selecting the potentially new processes

Selection Criterion

- Operating conditions
- Performance of catalyst
- Product sales and raw material costs
- Thermodynamic feasibility

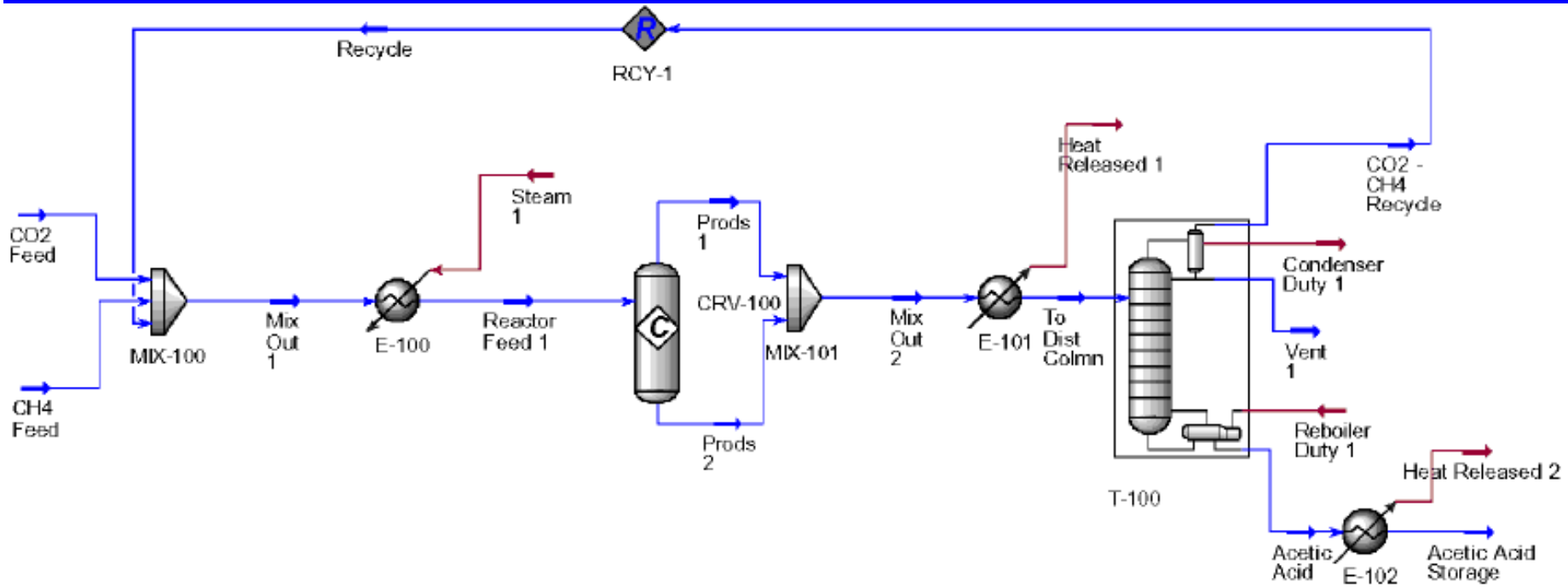
Example: Acetic Acid Process

- Commercial process
- Carbonylation of methyl alcohol
- $CO + CH_3OH \rightarrow CH_3COOH$
- $\Delta H^o = -135$ kJ/mol, $\Delta G^o = -87$ kJ/mol
- Operating conditions: 450K, 30 bar
- Hydrogen iodide catalyst
- Complete conversion of methanol

Example: Acetic Acid Process (Continued)

- New experimental study
- $CH_4 + CO_2 \rightarrow CH_3COOH$
- $\Delta H^o = 36$ kJ/mol, $\Delta G^o = 71$ kJ/mol
- Operating conditions: 350K and 25 bar
- Vanadium catalyst
- 97% conversion of methane

HYSYS Process Flow Diagram for Acetic Acid Process



Selected Studies

- Eighty-six experimental studies reviewed
- Seventy experimental studies compared
- Twenty potentially new process selected

Selected Studies (Continued)

- Twenty processes selected include
  - Five new processes for methanol
  - Two new processes for ethanol, styrene, and propylene
  - Four new processes for hydrogen and carbon monoxide
  - One new process each for DME, formic acid, acetic acid, methylamines, and graphite

HYSYS Simulations

- Based on existing production capacities
- Obtain energy requirements
- Obtain stream flow rates

Value Added Economic Model

- Profit = Σ Product Sales – Σ Raw Material Costs - Σ Energy Costs
- Product selling prices and raw material costs were obtained from literature
- HP steam and cooling water required were estimated using information from HYSYS
- Stream flow rates obtained from HYSYS flow sheet

Selection Based on Value Added Economic Profit

- Only the best process for each product was selected
- Only processes with profit were considered

Integration into Superstructure

- Twenty processes simulated
- Eleven processes selected based on value added economic model
- Integrated into the superstructure using the System

Processes Integrated into Superstructure

Product	Synthesis Route	Value Added Profit (cents/kg)
Methanol	CO_2 hydrogenation	5.8
Ethanol	CO_2 hydrogenation	33.6
Dimethyl Ether	CO_2 hydrogenation	69.6
Formic Acid	CO_2 hydrogenation	65.0
Acetic Acid	From CH_4 and CO_2	98.0
Styrene	Ethylbenzene dehydrogenation	11.0

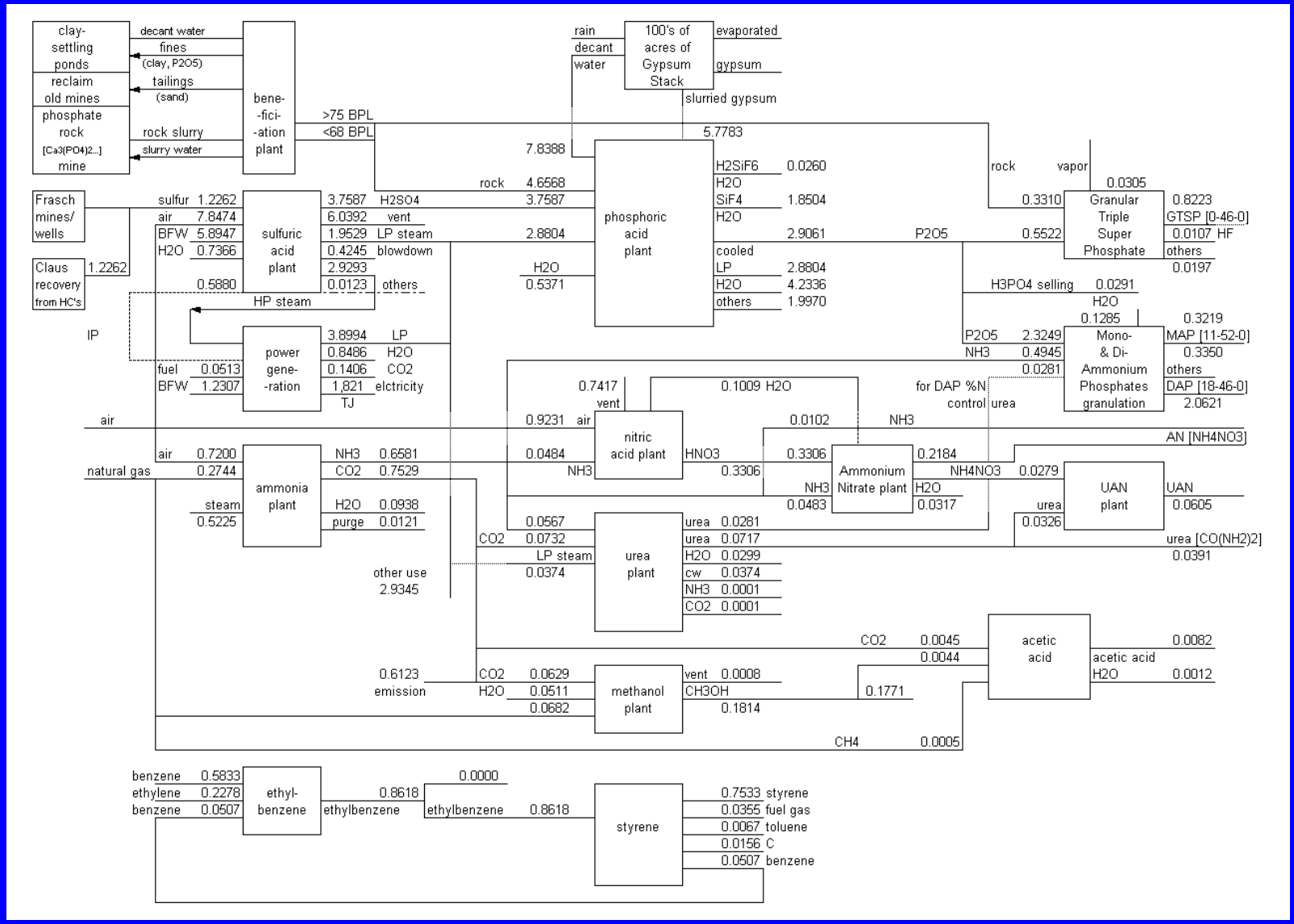
Processes Integrated into Superstructure (Continued)

Product	Synthesis Route	Value Added Profit (cents/kg)
Methylamines	From CO_2, H_2, and NH_3	124.0
Graphite	CO_2 reduction	65.5
Hydrogen	Methane reforming	17.4
Propylene	Propane dehydrogenation	4.4
Propylene	Propane dehydrogenation with CO_2	2.4

Application of the System to Chemical Complex in the Lower Mississippi River Corridor

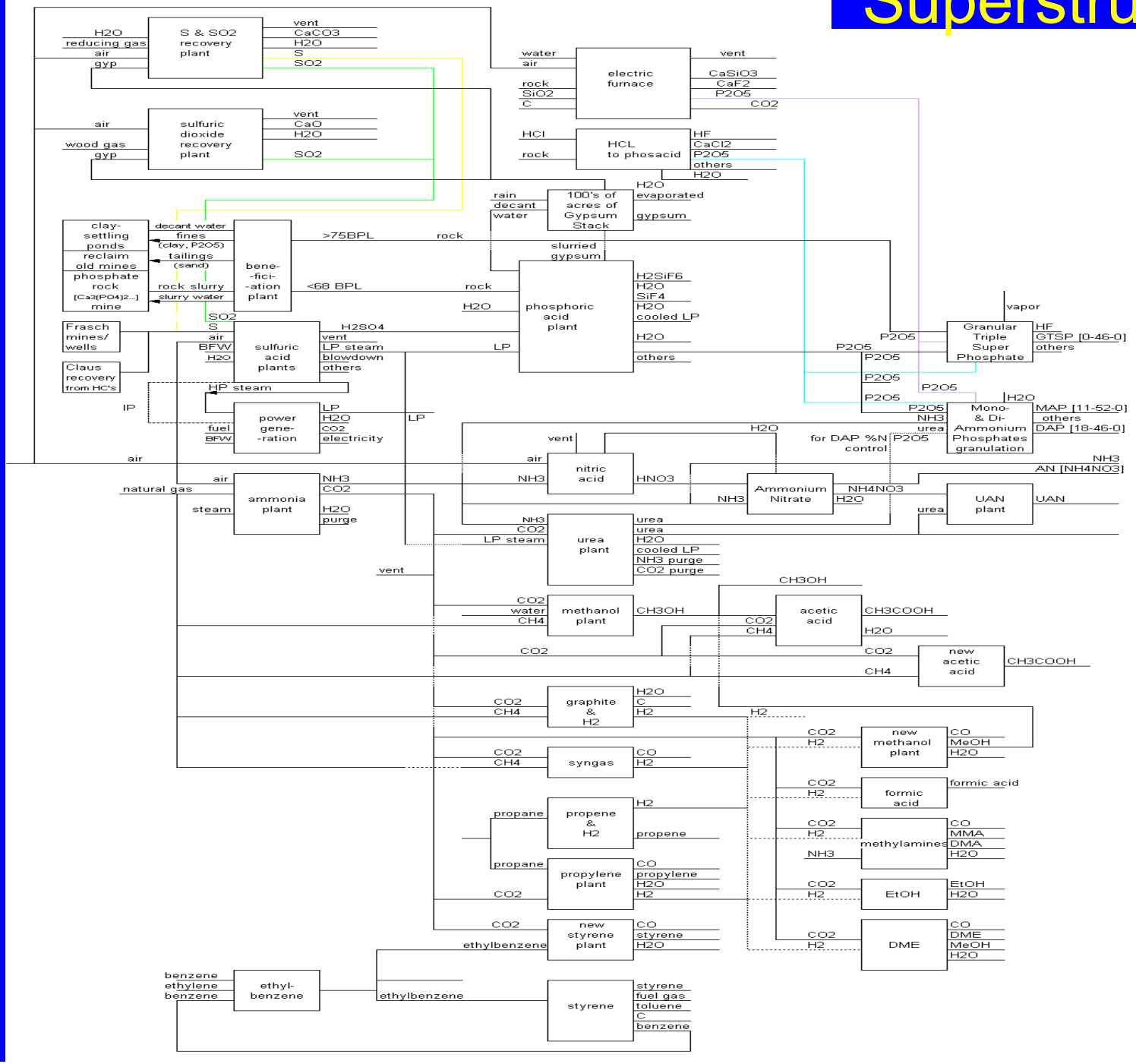
- Base case
- Superstructure
- Optimal structure

Base Case of Actual Plants



Plants in the lower Mississippi River Corridor, Base Case. Flow Rates in Million Tons Per Year

Superstructure



Processes in the Superstructure

Plants in the Base Case

- Ammonia
- Nitric acid
- Ammonium nitrate
- Urea
- UAN
- Methanol
- Granular triple super phosphate
- MAP & DAP
- Contact process for Sulfuric acid
- Wet process for phosphoric acid
- Acetic acid
- Ethylbenzene
- Styrene

Plants Added to form the Superstructure

- Electric furnace process for phosphoric acid
- HCl process for phosphoric acid
- SO_2 recovery from gypsum
- S & SO_2 recovery from gypsum
- Acetic acid from CO_2 & CH_4
- Graphite & H_2
- Syngas from CO_2 & CH_4
- Propane dehydrogenation
- Propylene from propane & CO_2
- Styrene from ethylbenzene & CO_2
- Methanol from CO_2 & H_2
- Formic acid
- Methylamines
- Ethanol
- Dimethylether

Superstructure Characteristics

Options

- Three options for producing phosphoric acid
- Two options for producing acetic acid
- Two options for recovering sulfur and sulfur dioxide
- Two options for producing styrene
- Two options for producing propylene
- Two options for producing methanol

Mixed Integer Nonlinear Program

785 continuous variables

20 integer variables

718 equality constraint equations for material and energy balances

58 inequality constraints for availability of raw materials

demand for product, capacities of the plants in the complex

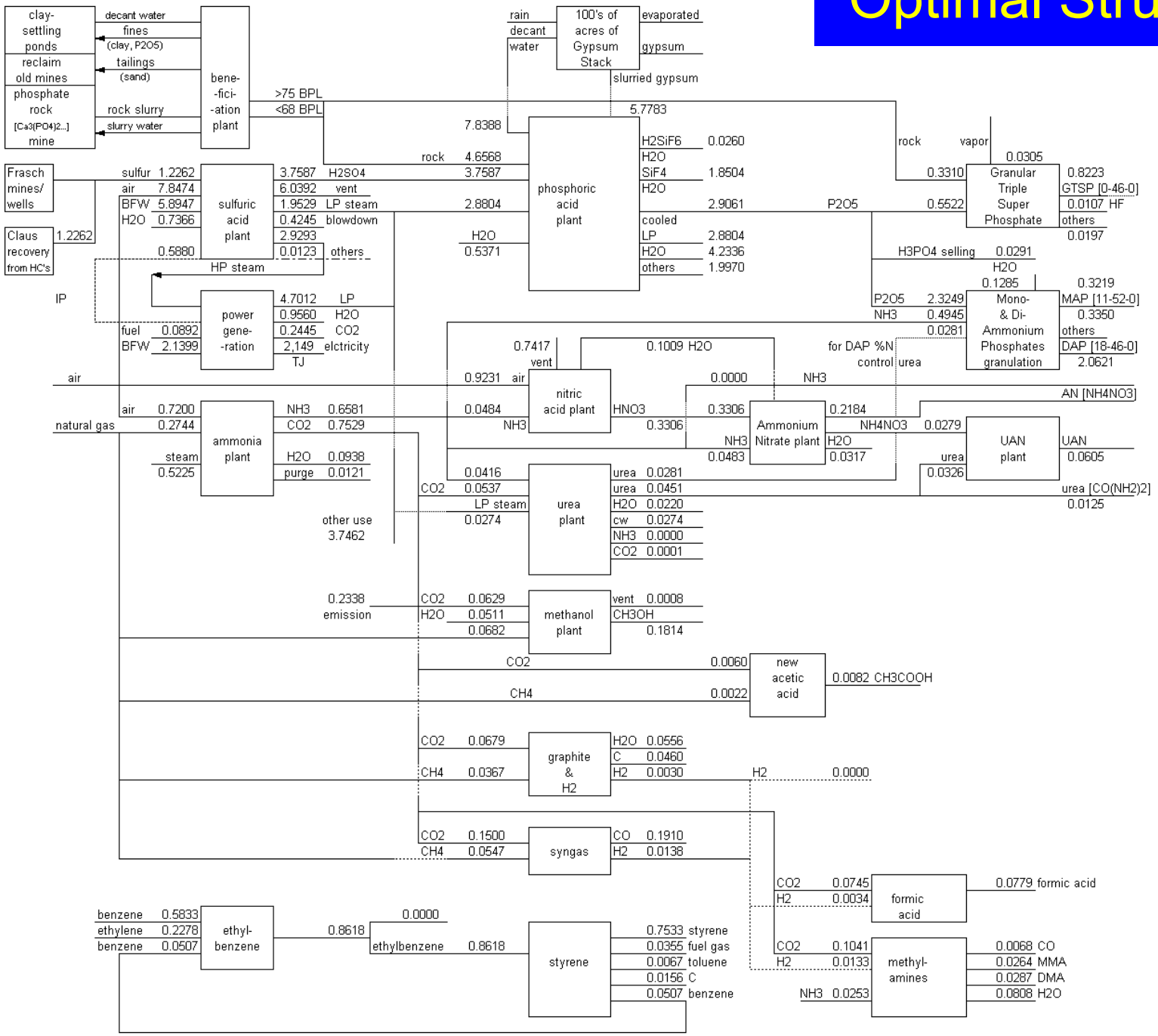
Raw Material and Product Prices

Raw Materials	Cost ($/mt)
Natural Gas	172
Phosphate Rock	
wet process	27
electrofurnace	24
HCl process	25
GTSP process	30
HCl	50
Sulfur	
Frasch	
Claus	
C electrofurnace	760
Ethylene	42
Benzene	38
Propane	257
	446
	163

Raw Materials	Cost ($/mt)
Market cost for short term purchase	1394
Reducing gas	
Wood gas	
Sustainable Costs and Credits	
Credit for CO_2 Consumption	6.50
Debit for CO_2 Production	3.25
Credit for HP Steam	634
Credit for IP Steam	10
Credit for gypsum	6.4
Consumption	5
Debit for gypsum Production	2.5
Debit for NO_x Production	1025
Debit for SO_2 Production	150

Products	Price ($/mt)
Ammonia	150
Methanol	300
Acetic Acid	1034
GTSP	142
MAP	180
DAP	165
NH_4NO_3	153
UAN	112
Urea	154
H_3PO_4	320
Ethanol	670
Ethylbenzene	551
Propene	240
CO	31
Graphite	882
H_2	796
Styrene	705
Toluene	238
Fuel Gas	596
Formic Acid	690
MMA	1606
DMA	1606
DME	946

Optimal Structure



Processes in the Optimal Structure

Plants in the Base Case

- Ammonia
- Nitric acid
- Ammonium nitrate
- Urea
- UAN
- Methanol
- Granular triple super phosphate
- MAP & DAP
- Contact process for Sulfuric acid
- Wet process for phosphoric acid
- Ethylbenzene
- Styrene

Not in the Base Case

- Acetic acid

New Plants in the Optimal Structure

- Acetic acid from CO_2 & CH_4
- Graphite & H_2
- Syngas from CO_2 & CH_4
- Formic acid
- Methylamines

Plants Not in the Optimal Structure

- Electric furnace process for phosphoric acid
- HCl process for phosphoric acid
- SO_2 recovery from gypsum
- S & SO_2 recovery from gypsum
- Propane dehydrogenation
- Propylene from propane & CO_2
- Styrene from ethylbenzene & CO_2
- Methanol from CO_2 & H_2
- Ethanol
- Dimethylether

Comparison of Base Case and Optimal Structure (Million $ / year)

	Base Case	Optimal Structure
Profit	378	529
Environmental Cost	334	349
Sustainable Cost	-18	-21

Zero Emission of CO_2 from Ammonia Plant
Comparison of Base Case and Optimal Structure
(Million $ / year)

	Base Case	Optimal Structure
Profit	378	469
Environmental Cost	334	315
Sustainable Cost	-18	-17

Zero Emission of CO_2 from NH_3 Plant Running at Full Capacity
Comparison of Base Case and Optimal Structure
(Million $ / year)

	Base Case	Optimal Structure
Profit	378	460
Environmental Cost	334	368
Sustainable Cost	-18	-24

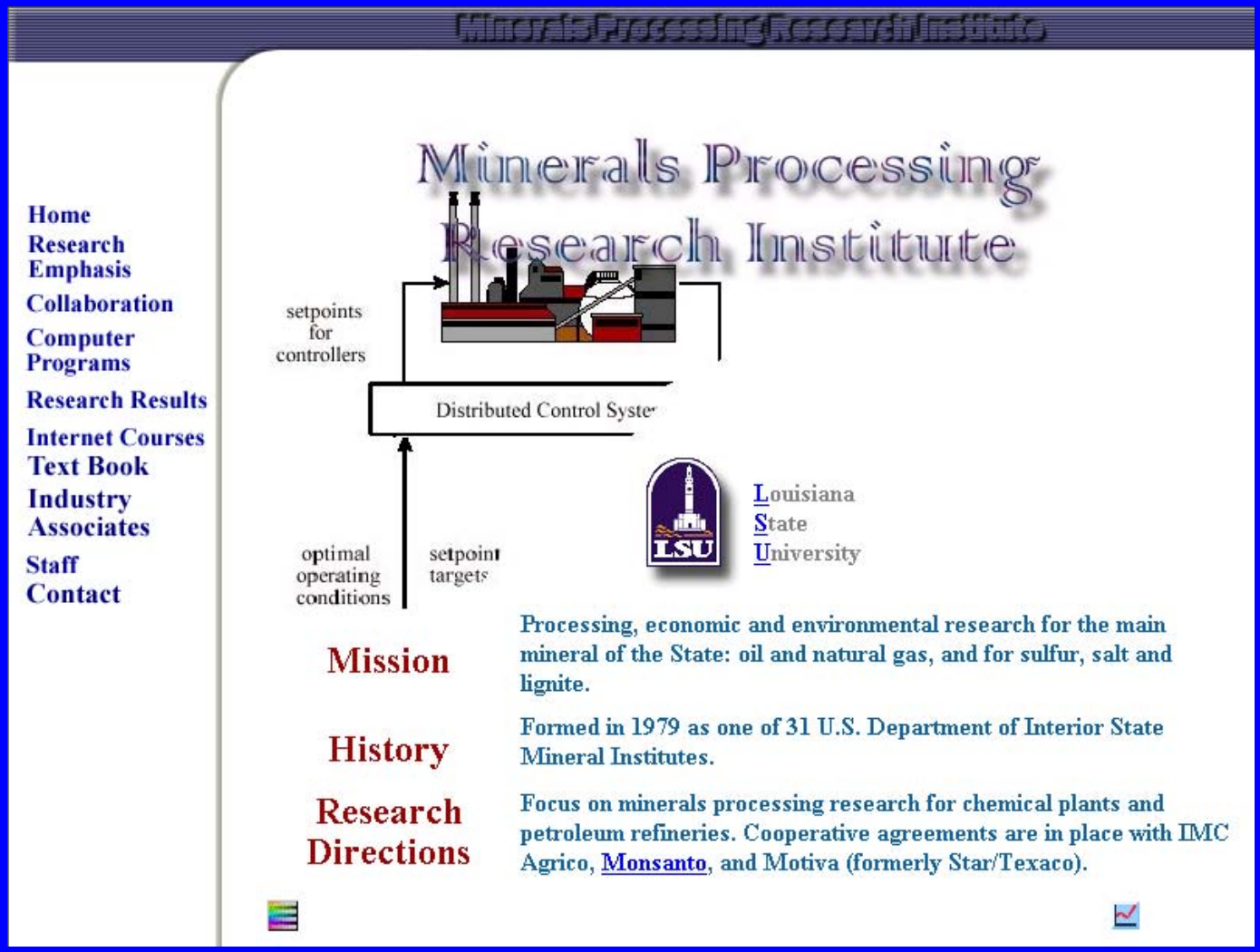
Conclusions

- A new methodology was developed for identifying potentially new processes
- Twenty potentially new processes were simulated using HYSYS and eleven were selected for integrating into the superstructure
- The System has been applied to a chemical complex in the lower Mississippi River corridor
- Value added model incorporated economic, environmental and sustainable costs.

Conclusions (Continued)

- An optimum configuration of plants was determined with increased profit and decreased sustainable cost.
- Based on these results, the System could be applied to other chemical complexes in the world.
- The System includes the program with users manuals and tutorials. These can be downloaded at no cost from the LSU Mineral Processing Research Institute's web site www.mpri.lsu.edu

LSU Mineral Processing Research Institute

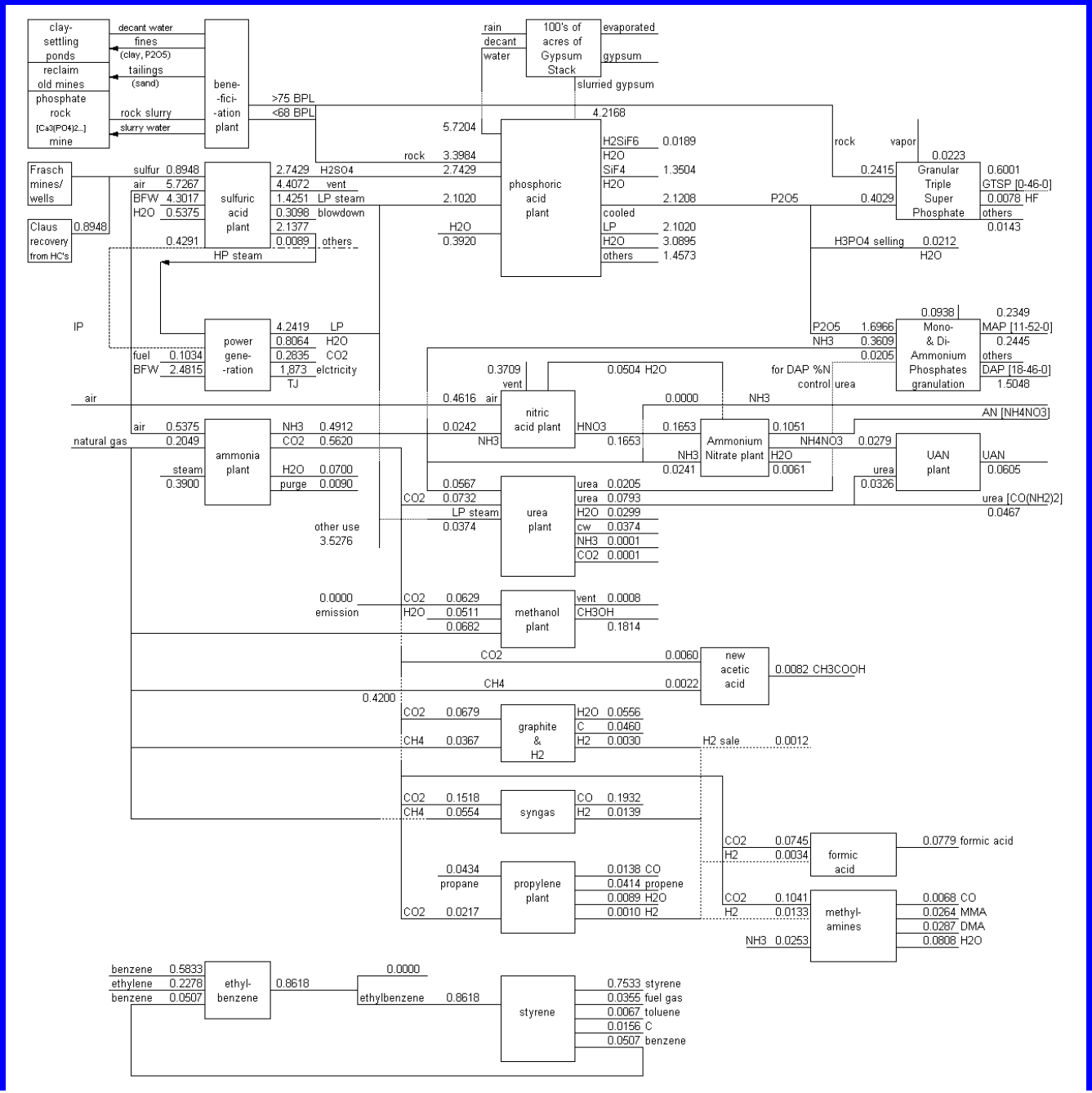


All of the information given in this presentation is available at www.mpri.lsu.edu

Comparison of Base Case and Optimal Structure

		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	energy	-21,405,665	energy
Plant name	Capacity (t/year)	Capacity	requirement	Capacity	requirement
	(upper-lower bounds)	(t/year)	(TJ/year)	(t/year)	(TJ/year)
Ammonia	329,030-658,061	658,061	3,820	658,061	3,820
Nitric acid	89,274-178,547	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	4,082-8,165	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
SO2 recovery from gypsum	902,208-1,804,417	na	na	0	0
S & SO2 recovery from gypsum	451,526-903,053	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	13,773	884
Propene & H2	20,896-41,791	na	na	0	0
Propene using CO2	20,714-41,429	na	na	0	0
New Styrene	181,118-362,237	na	na	0	0
New methanol	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	
Total energy requirement			4,028		6,786

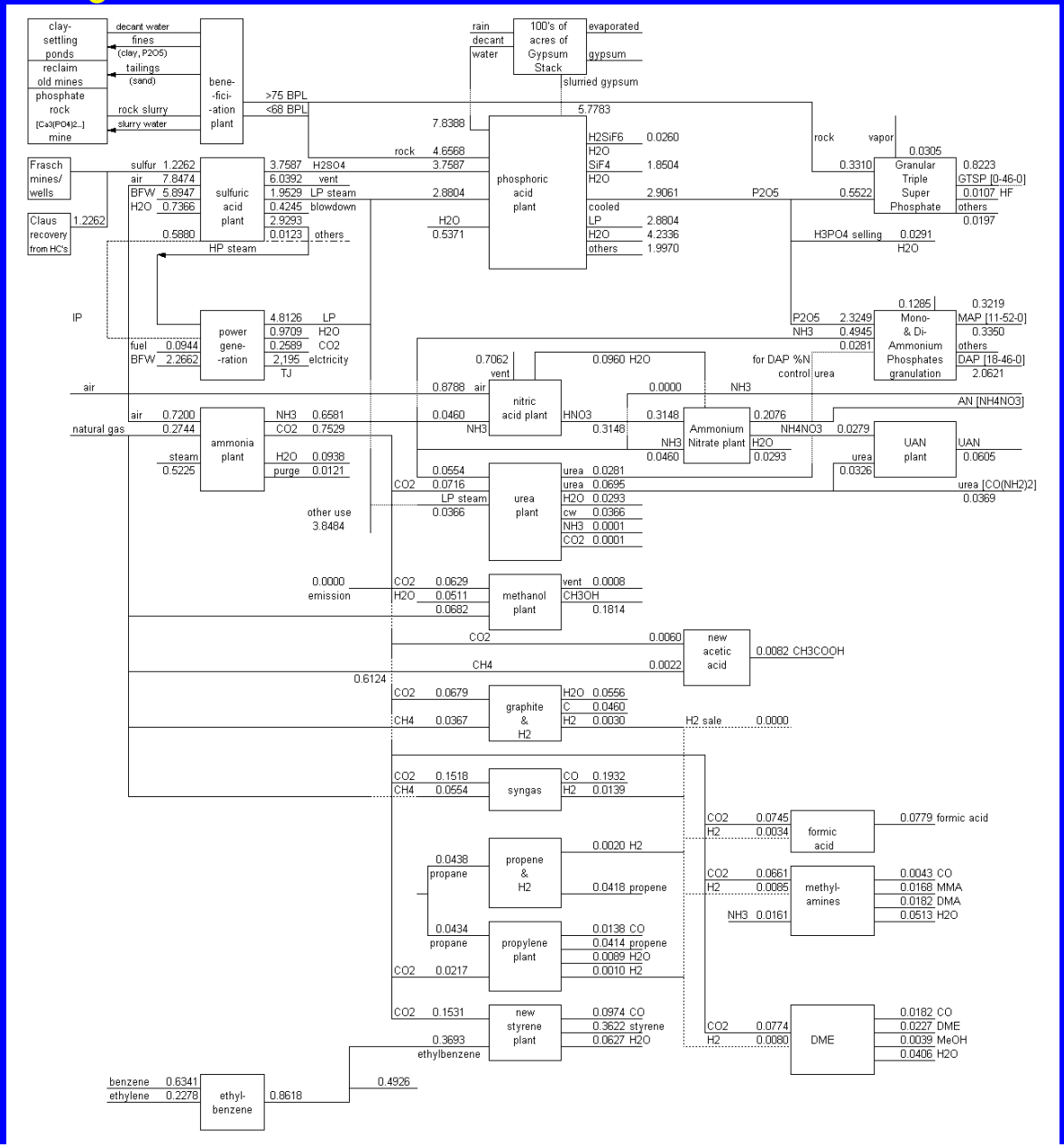
Optimal Structure of CO_2 Zero Emission from Ammonia Plant



Comparison of Base Case and Optimal Structure of Zero CO_2 Emission from Ammonia Plant

		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	energy	-17,037,558	energy
Plant name	Capacity (t/year)	Capacity	requirement	Capacity	requirement
	(upper-lower bounds)	(t/year)	(TJ/year)	(t/year)	(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
SO2 recovery from gypsum	902,208-1,804,417	na	na	0	0
S & SO2 recovery from gypsum	451,526-903,053	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	0	0
Propene using CO2	20,714-41,429	na	na	41,429	408
New Styrene	181,118-362,237	na	na	0	0
New methanol	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	
Total energy requirement			4,028		7,689

Optimal structure of Zero Emission of CO_2 from NH_3 Plant Running at Full Capacity



Comparison of Base Case and Optimal structure of Zero Emission of CO_2 from NH_3 Plant Running at Full Capacity

		Base case		Optimal structure	
Profit (U.S.$/year)		378,325,617		459,608,035	
Environmental cost (U.S.$/year)		334,403,783		368,257,342	
Sustainability cost (U.S.$/year)		-18,039,196	energy	-23,633,460	energy
Plant name	Capacity (t/year)	Capacity	requirement	Capacity	requirement
	(upper-lower bounds)	(t/year)	(TJ/year)	(t/year)	(TJ/year)
Ammonia	329,030-658,061	658,061	3,820	658,061	3,820
Nitric acid	89,274-178,547	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	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	-756
Styrene	385,554-771,108	753,279	3,318	0	0
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
SO2 recovery from gypsum	902,208-1,804,417	na	na	0	0
S & SO2 recovery from gypsum	451,526-903,053	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	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	
Total energy requirement			4,028		7,169

Commercial Pipelines for CO_2

- Ashland Chemical's methanol plant ran on CO_2 piped from an ammonia plant about 13 miles away.
- At least two across-the-fence CO_2 pipelines have been built to keep a urea plant and methanol plant running while its normal-CO_2-source ammonia plant was down for maintenance.
- The 183-mile Denbury CO_2 pipeline distributes CO_2 from a volcanic formation near Jackson MS to many MS oilfields and to some chemical production. This line extends into Louisiana and could be a key in sustaining urea, methanol, etc. production in LA.
- There are many other oilfield-servicing CO_2 pipelines in the MS-UT-NM triangle. Twelve of these lines total total 1,1016 miles. The CO_2 source for these lines is 'high-CO_2-content natural gas'.

Estimation of Utilities

- Using information from HYSYS flow sheet
  - Obtain energy supplied
  - Obtain energy liberated
- Assumptions
  - HP steam used to supply energy
  - Cooling water used to absorb energy

Economic Results for HYSYS Simulated Acetic Acid Process

Product/Raw Material	Flow Rate from HYSYS Simulation (kg/hr)	Cost/Selling Price ($/kg)
Carbon Dioxide	684.8	0.003
Methane	249.1	0.172
Acetic Acid	932.6	1.034
HP Steam	766.0	0.00865
Cooling Water	13,730	6.7×10^{-6}
Value Added Profit	$ 913/hr	98 cents/kg

Original Contribution

- No integrated set of tools, methodology or programs to perform a consistent and accurate evaluation of new plants and existing processes.
- No method to evaluate the sustainability development of the chemical complex.
- The objective of the System is to have a methodology to integrate new plants into the existing infrastructure of plants in a chemical production complex. The results will lead to new processes that manufacture products from greenhouse gases and use cogeneration for efficient steam and power generation.
- The Chemical Complex and Cogeneration Analysis System will give corporate engineering groups new capability to design energy efficient and environmentally acceptable plants and have new products from greenhouse gases.