

## Integrated Chemical Complex and Cogeneration Analysis System: Energy Conservation and Greenhouse Gas Management Solutions

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Abstract:

The Chemical Complex and Cogeneration Analysis System is an advanced technology for energy conservation and pollution prevention. This System combines the Chemical Complex Analysis System with the Cogeneration Design System. The Chemical Complex (Multi-Plant) Analysis System is a new methodology that has been developed with EPA support 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. The Cogeneration Design System examines corporate energy use in multiple plants and determines the best energy use based on economics, energy efficiency, regulatory emissions and environmental impacts from greenhouse gas emissions. It uses sequential layer analysis to evaluate each plant's current energy use as at an acceptable level or cost-effective improvements are possible. It includes cogeneration as a viable energy option and evaluates cogeneration system operating optimally. Also, a region wide analysis is made on impact of merchant power plants and tightening emission standards on the region's energy base.

The System uses a Windows graphical user interface. The process flow diagram for the complex is constructed, and equations for material and energy balances, rate equations and equilibrium relations for the plants entered and stored in the Access database using interactive data forms. Also, process unit capacities, availability of raw materials and demand for product are entered in the database. These equations give a complete description to predict the operations of the plants. The format for the equations is the GAMS programming language that is similar to Excel. The input includes incorporating new plants that use greenhouse gases as raw materials.

The System has been applied to an agricultural chemical production complex in the Baton Rouge-New Orleans Mississippi river corridor. Ammonia plants in this complex produce an excess of surplus of 0.65 million tons per year of high quality carbon dioxide that is being exhausted to the atmosphere. A new catalytic process that converts carbon dioxide and methane can use some of this excess, and preliminary results 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  $\text{NO}_x$  and 49,100 tons per year in carbon dioxide emissions.

This System is to be used by corporate engineering groups for regional economic, energy, environmental and sustainable development planning to accomplish the following: energy efficient and environmentally acceptable plants and new products from greenhouse gases. 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.

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](http://www.mpri.lsu.edu).

## Introduction

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

A regional methodology for cogeneration and conversion of greenhouse gases to products using existing chemical production complexes will assist in overcoming these limitations. The methodology is available in individual components, and these components are being integrated into the Chemical Complex and Cogeneration Analysis System, simply called the System in this paper. This technology is being applied to the chemical production complex in the Baton Rouge-New Orleans Mississippi River corridor initially which contains over 150 chemical plants that consume about 1.0 quad ( $1 \times 10^{15}$  Btu/yr) of energy and generate about 215 million pounds of pollutants annually. Its capability is being demonstrated on companies' plants for increased energy efficiency, reduced greenhouse gas emissions and integration of new plants based on greenhouse gases as raw materials. The System includes programs with users manuals and tutorials that can be downloaded at no cost from the LSU Mineral Processing Research Institute's web site [www.mpri.lsu.edu](http://www.mpri.lsu.edu).

## Greenhouse Gases as Raw Materials

The potential reaction pathways to useful materials from carbon dioxide is illustrated in the diagram shown in Figure 1 from Creutz and Fujita, 2000. Also, further details for the utilization of carbon dioxide is given by Inui, et al., 1998, Sullivan, 1993 and Inoue and Yamazaki, 1982. In essence, carbon dioxide can be used as the whole molecule in reactions, as a carbon source and as

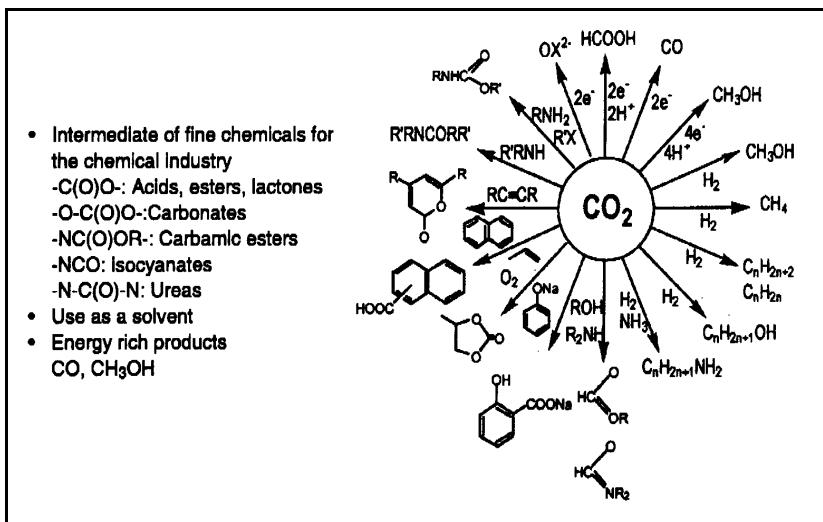


Figure 1 Utilization of Carbon Dioxide in Synthetic Chemistry, from Creutz and Fujita, 2000.

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 isocyanates supplanting phosgene.

## **Cogeneration/Combined Heat and Power (CHP)**

Cogeneration for combined electricity and steam production (CHP) is a means of substantially reducing energy costs and greenhouse gas emissions in energy intensive chemical plants, oil refineries and paper industries. The average operating efficiency of existing power plants is 33% conversion of energy to electricity while the operating efficiency of a CHP utility plant is 77%. There are many issues affecting the movement from conventional power generation to cogeneration, and some include capital investments in existing plants and new merchant plants, regulatory restraints, air pollution non-attainment areas, regional power shortages, and volatile commodity markets.

Numerous studies by academics and research institutes alike have repeatedly shown that U.S. from the 1960s - 1980s, there have been very few technological improvements at utility generating facilities. These regulated monopolies have had little incentive to take advantage of technological advances that can double today's average efficiency for power, or triple that efficiency when waste heat is recovered. Traditional power plants operate at heat rates over 10,000 BTUs of energy per kWh. Some units, operating five months out of the year to serve a retail peak load, are operating at a grossly inefficient heat rate of 28,500 BTU of energy per kWh. Most CHP applications at large industrial facilities, operate at between 5,000 to 6,000 BTUs of energy per kWh.

Another major consideration is that emissions regulations are tightening throughout the country. Until recently, power plants could be permitted with virtually no limits on NOx emissions. Now, it is difficult to permit a plant with NOx emissions higher than 10 ppm in many areas of the country. Within a few years it is expected that the NOx standard will drop to between 3 and 5 ppm. In addition, five other items are measured in most clean air legislation: ozone, particulate matter, carbon monoxide, sulfur dioxide and lead. NOx is considered a pre-cursor to ozone and is often singled out as the primary target for reductions.

CHP goes a long way in reducing NOx and other pollutants from power plants. The average utility power plant emits approximately 4.9 lbs of NOx for every megawatt hour (MWH) while a five MW gas turbine produces 0.167 lbs of NOx per MWH. Regarding CO<sub>2</sub> emissions, the average utility plant produces about 1.06 tons of CO<sub>2</sub> per MWH, while a five MW gas turbine emits about 0.30 tons of CO<sub>2</sub> per MWH.

## **Related Work and Programs**

Aspen Technology of Cambridge, Massachusetts is the worldwide leading modeling technology company, and they have programs for plant design, supply chains and manufacturing. These programs are licensed to a company for a specific application, but they do not have a system comparable to the one described here, as yet.

The DOE web site, [www.oit.doe.gov/bestpractices](http://www.oit.doe.gov/bestpractices), describes Best Practices, a program of the Office of Industrial Technologies (OIT), that works with industry to identify plant-wide

opportunities for energy savings and process efficiency. This web site describes resources to help a company manage energy needs, including software tools and databases that help analyze steam, compressed air, motor, and process heating systems.

The EPA web site, [www.epa.gov/opptintr/greenengineering](http://www.epa.gov/opptintr/greenengineering), lists software to provide academia and industry a compilation of risk assessment software tools used by EPA, such as those for risk screening, hazard, exposure, and fate estimation. Most of these can be downloaded directly at no cost. This compilation also includes some commercially available risk assessment/pollution prevention tools. These tools can assist engineers in the prioritization, design, and selection of greener processes and products. Also, there are tables that list software in the recently published textbook sponsored by EPA, *Green Engineering: Environmentally Conscious Design for Chemical Processes* (Allen and Shonnard, 2002).

### **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 accomplish the following:

- Energy efficient and environmentally acceptable plants
- 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 efficiency and pollution prevention using on-line optimization, pinches analysis, chemical reactor analysis, pollution assessment and process simulation.

The structure of the System is shown in Figure 2, 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. The integrated cogeneration sequential layer analysis determines cost effective improvements for individual plants using heat exchanger network analysis and cogeneration opportunities. Then these results are used to determine the optimum complex configuration and utilities integrated with the plants (Output in Figure 2).

Plants in a production complex can occupy a large portion of a state or adjacent states, and the results are used for a region wide analysis to access the impact of merchant power plants and tightening emission standards on the region's energy base.

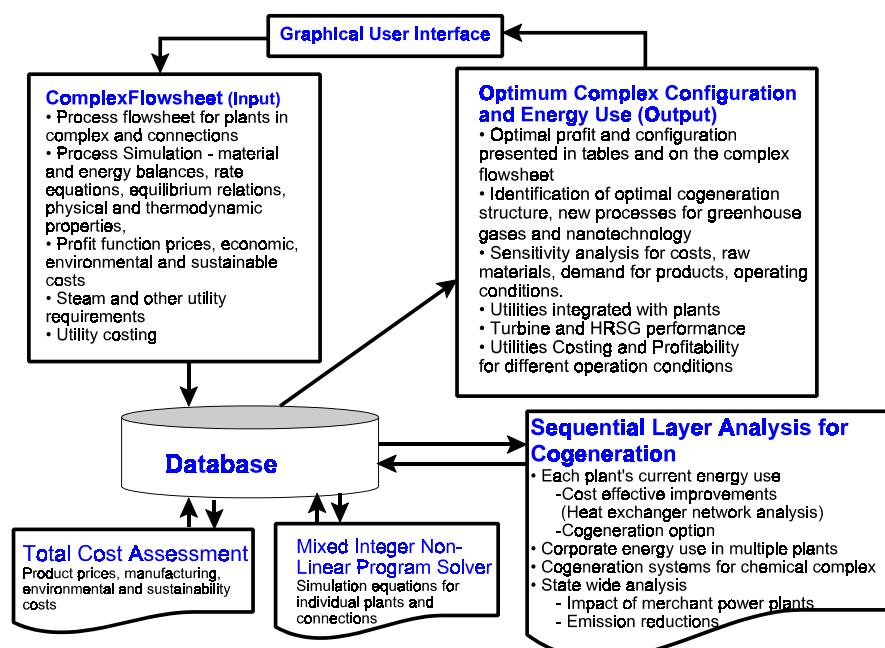


Figure 2 Structure of the Chemical Complex and Cogeneration Analysis System

process flow diagram for the complex is constructed, and equations for the process units and variables for the streams connecting the process units are entered and stored in an Access database using interactive data forms. Material and energy balances, rate equations and equilibrium relations for the plants are entered as equality constraints using the format of the GAMS programming language that is similar to Excel and stored in the database. Process unit capacities, availability of raw materials and demand for product are entered as inequality constraints and stored in the database. The System takes the equations in the database and writes and runs a GAMS program to solve the mixed integer nonlinear programming problem for the optimum configuration of the complex. Then the important information from the GAMS solution is presented to the user in a convenient format, and the results can be exported to Excel, if desired. Features for developing flowsheets include adding, changing and deleting the equations that describe units and streams and their properties. Usual Windows features include cut, copy, paste, delete, print, zoom, reload, update and grid, among others. A typical window for entering process information is shown in Figure 3, and in this figure a material balance equation for the acetic acid process, U15, has been entered as an equality constraint. Typical output from the cogeneration analysis is shown on the diagram in Figure 4 for the results from the prototype. A detailed description of these operations will be provided in an interactive user's manual with help files and a tutorial.

The Chemical Complex and Cogeneration Analysis System combines the Chemical Complex Analysis System with the Cogeneration Design System. The Chemical Complex (Multi-Plant)

Prior to optimization of the chemical complex, the analysis is validated using a base case of existing plants. This is done to ensure this analysis matches the performance of the actual plants.

The prototype is an interactive Windows program that integrates existing programs. All interactions with the System are through a graphical user interface designed and implemented with Visual Basic. As shown in the diagram, (Figure 2) the

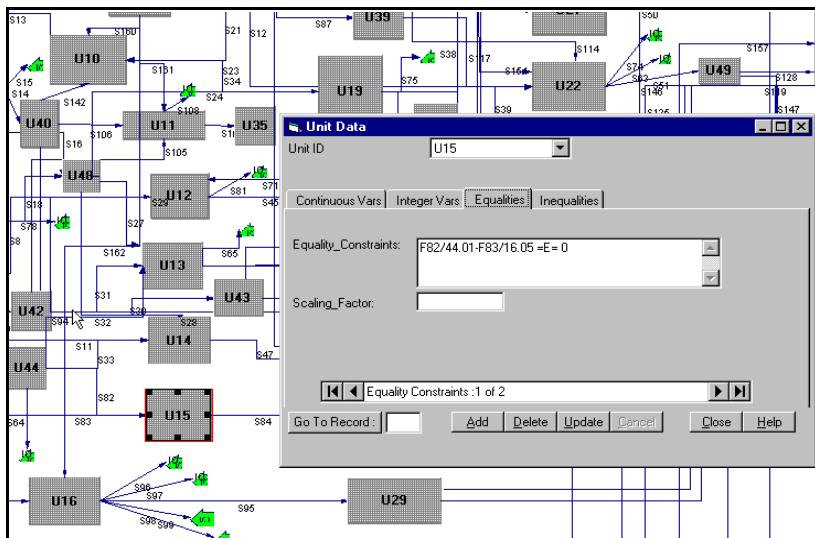


Figure 3 Illustration of Input to the System for Unit Data

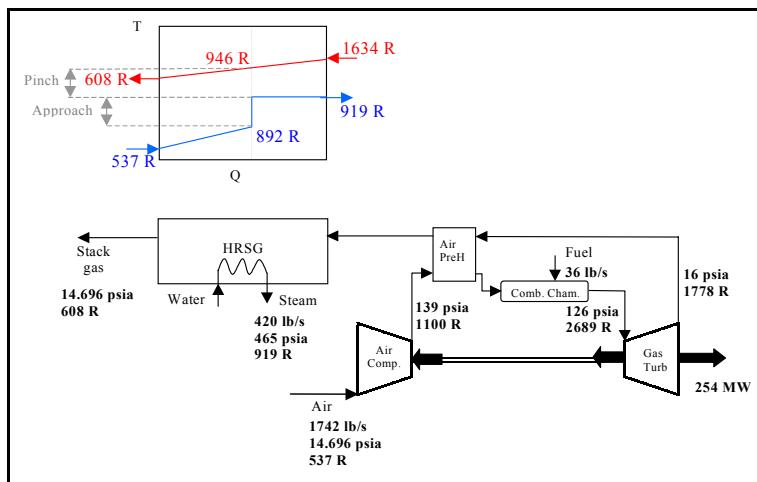


Figure 4 Typical Cogeneration Results Shown on the CHP Diagram in the System

Analysis System is a new methodology 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. The Cogeneration Design System examines corporate energy use in multiple plants and determines the best energy use based on economics, energy efficiency, regulatory emissions and environmental impacts from greenhouse gas emissions. It uses sequential layer analysis to evaluate each plant's current energy use as at an acceptable level or cost-effective improvements are possible. It includes cogeneration as a viable energy option and evaluates cogeneration system operating optimally. Also, a region wide analysis is made on impact of merchant power plants and tightening emission standards on the region's energy base.

## Application of the Chemical Complex and Cogeneration Analysis System

Results using the Chemical Complex Analysis System has 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 this agricultural chemical production complex in the Baton Rouge-New Orleans Mississippi river corridor. (Hertwig, et al., 2002). Here, ammonia plants produce 0.8 million tons per year of carbon dioxide, and methanol and urea plants consume 0.15 million metric tons per year of carbon dioxide. **This leaves a surplus of 0.65 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 36,700 tons per year of this carbon dioxide could be economically converted to acetic acid in a 100 million pound per year plant. This plant was included in the chemical production complex that used a new catalytic process for the direct conversion of carbon dioxide and methane to acetic acid (Taniguchi, 1998). Other potential processes for carbon dioxide use include adipic acid, dimethyl ether (*Chemical Engineering*, 2001) and cyclic carbonates (*C&E News*, 2001).

Table 7 Production Costs for Acetic Acid (cents per kg)

Source Moulijn, et al., 2001

Plant	Methanol	Methane
<u>Production Cost</u>	<u>Carbon Monoxide</u>	<u>Carbon Dioxide</u>
Raw Materials	21.6	21.6
Utilities	3.3	1.7
Labor	1.2	1.2
Other (capital, catalyst)	<u>10.1</u>	<u>10.1</u>
Total Production Cost	36.2	34.6
Current market price	79 cents per kg	

A comparison of the conventional process for acetic acid in the agricultural chemical production complex was made to the new catalytic process for the direct conversion of carbon dioxide and methane to acetic acid. This new plant was included in the optimal solution using the prototype of the System and the conventional one was not included. In the

conventional process 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 methane in excess carbon dioxide. 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 (Moulijn, , et al., 2001). This process includes a reactor, a flash drum and four distillation columns. The new process requires a catalytic reactor operating at 350 K and 25 bar for a 97% conversion of methane in excess carbon dioxide, and equipment include the reactor and a distillation column to separate the unreacted carbon dioxide for recycle and acetic acid product.

For a conservative estimate, the economic, energy and environmental benefits were evaluated on the savings associated with the acetic acid water separation which is not required in the new plant. In Table 1 the production costs are itemized from Moulijn, 2001, and the raw material, labor and capital cost should be comparable for the conventional (methanol carbon monoxide) and new (methane carbon dioxide) plants if not less for the new plant. A typical 100 million pound per year plant was used as a basis. There are eleven companies producing acetic acid in North America with plants of capacities from 44 to 2,000 million pounds per year with a total capacity of 5,544 million pounds per year, and demand is growing at 3% per year (ChemExpo Chemical Profile Acetic Acid, 1998).

The utilities reduction was based on a steam savings of 2.5 kg steam per kg of acetic acid producing commercial grade acetic acid rather than dry acetic acid. For a 100 million pound per year acetic acid plant there was a \$750,000 reduction in utilities costs for process steam for the new

plant compared to the conventional plant. The energy savings from not having to produce this steam was 275 trillion BTUs per year. Also, there was a reductions in NO<sub>x</sub> emissions of 3.5 tons per year base on steam and power generation by cogenetation which is significantly less than if a conventional was used. In addition, the carbon dioxide reduction from the steam production was 12,600 tons per year, and the total carbon dioxide reduction from converting it to a useful product (36,700 tons per year) and reduced energy generation was 49,100 tons per year.

## Conclusions

The System has been applied to an agricultural chemical production complex in the Baton Rouge-New Orleans Mississippi river corridor. A new catalytic process that converts carbon dioxide and methane can use excess carbon dioxide 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<sub>x</sub> and 49,100 tons per year in carbon dioxide emissions. These results are for one new chemical plant 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 nationwide.

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# Integrated Chemical Complex and Cogeneration Analysis System: Energy Conservation and Greenhouse Gas Management Solutions

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This is a joint industry-university project sponsored by the Gulf Coast Hazardous Substance Research Center.

# Outline

- Introduction
- Greenhouse gases
- Cogeneration
- Related work and programs
- Chemical Complex and Cogeneration Analysis System
- Results
- Conclusions and future work

This gives an outline of the presentation. First, some background information will be given to put this work in perspective.

# 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

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.

There will be greenhouse gas emission limitations. These are voluntary now and could become mandatory in the future.

# 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

There are opportunities to use greenhouse gases as raw materials and cogeneration in new, energy-efficient processes.

The Chemical Complex and Cogeneration Analysis System is a methodology for designing plants that converts greenhouse gases into new products using existing chemical production complexes and that uses cogeneration for efficient steam and power generation.

This technology is being applied to the chemical production complex in the lower Mississippi River corridor that contains over 150 chemical plants that consume about 1.0 quad ( $1 \times 10^{15}$  Btu/yr) of energy and generate about 215 million pounds of pollutants annually.

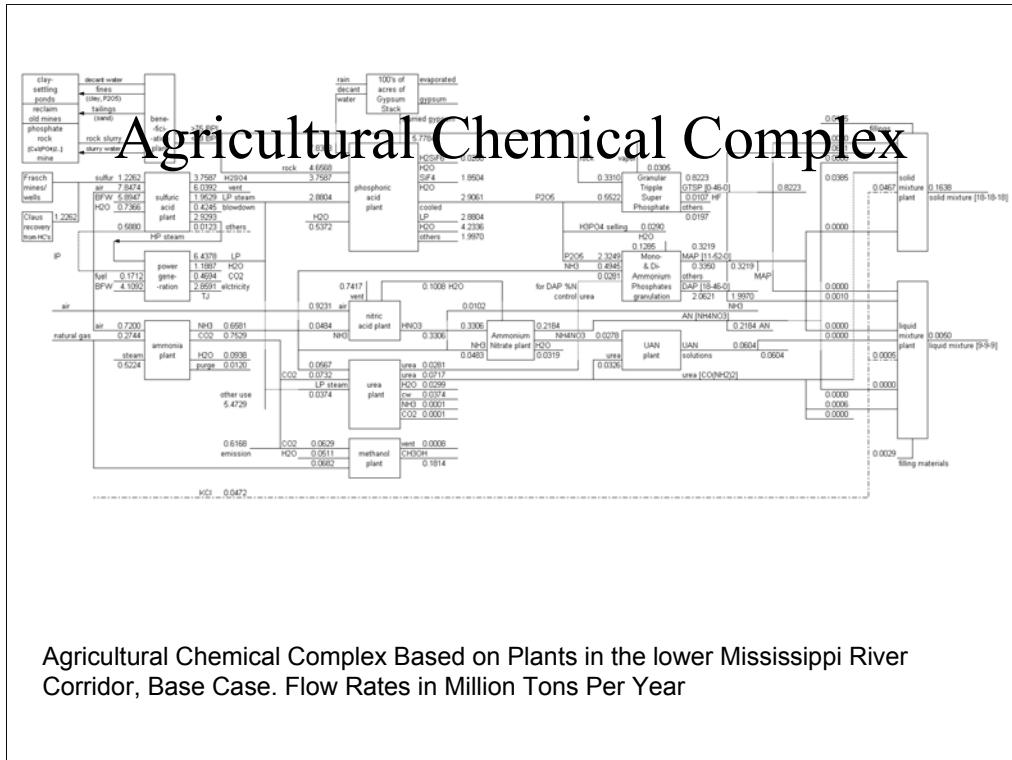
## Chemical Complex and Cogeneration Analysis System

### Objective

- Give corporate engineering groups new capability to design:
  - Energy efficient and environmentally acceptable plants
  - New processes for products from greenhouse gases

The objective of the System is to have a methodology to integrate new plants into the existing infrastructure of plants in a chemical complex. The results will be 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.

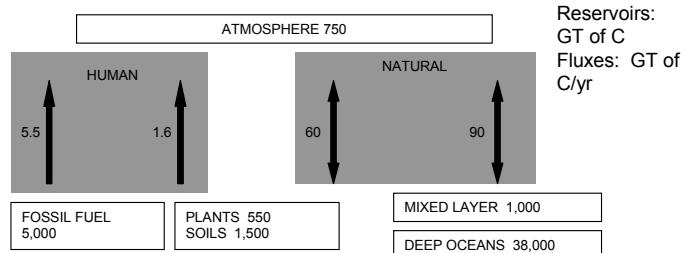


The agricultural chemical complex in the lower Mississippi river corridor serves as a base case used with the System. This is a process flow diagram for the existing plants in the lower Mississippi River Corridor that make up an agricultural chemical complex. It was developed by Tom Hertwig of IMC Agrico. Each block represents several plants. For example, the sulfuric acid production unit contains five plants owned by two companies. There are ten production units plus associated utilities for power, steam and cooling water and facilities for waste treatment.

In this complex ammonia plants produce 0.8 million tons per year, and methanol and urea plants consume 0.15 million tons per year of this carbon dioxide. The 0.65 million tons per year of surplus high purity carbon dioxide is exhausted to atmosphere. This excess carbon dioxide is available in pipelines that can be sent to new plants that use carbon dioxide as a raw material for new products.

More details about this base case will be provided in subsequent slides.

# CO<sub>2</sub> Sources and Cycle

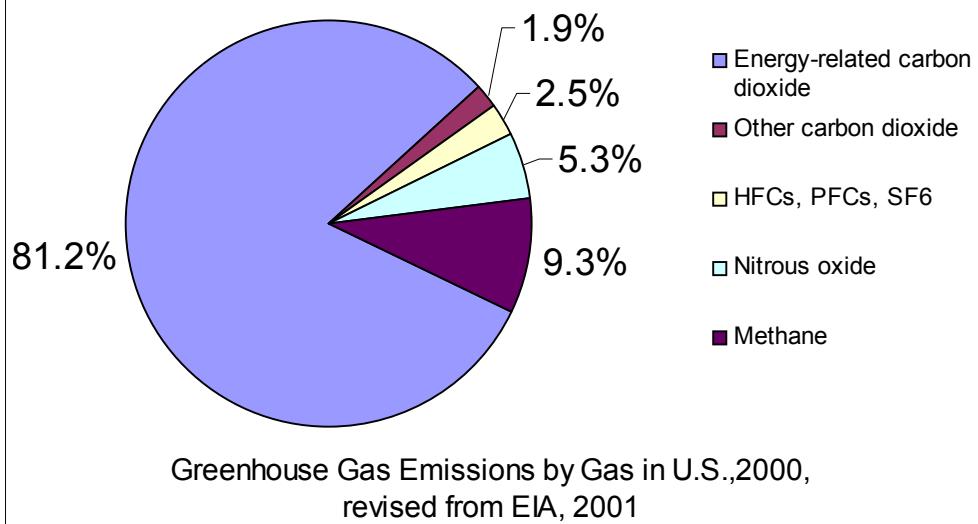


The Carbon Cycle, from IPCC (1995)

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

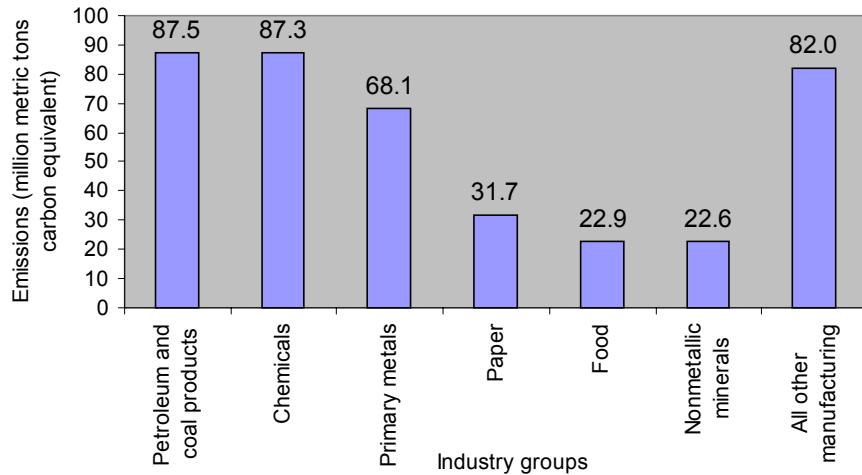
This information from IPCC provides an overview of carbon dioxide sources and cycles in the atmosphere. It shows that 5.5 gigaton per year are added to the atmosphere from burning fossil fuels.

## Greenhouse Gas Emissions



This information lists the composition of emissions for greenhouse gases. Carbon dioxide is the dominant species, and it is 81% of the total emissions.

# CO<sub>2</sub> Emissions from Industries



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

This information shows the distribution of carbon dioxide emissions by selected manufacturing industries in 1998 in the U.S.. 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 (1998).

## Carbon Dioxide Emissions and Utilization

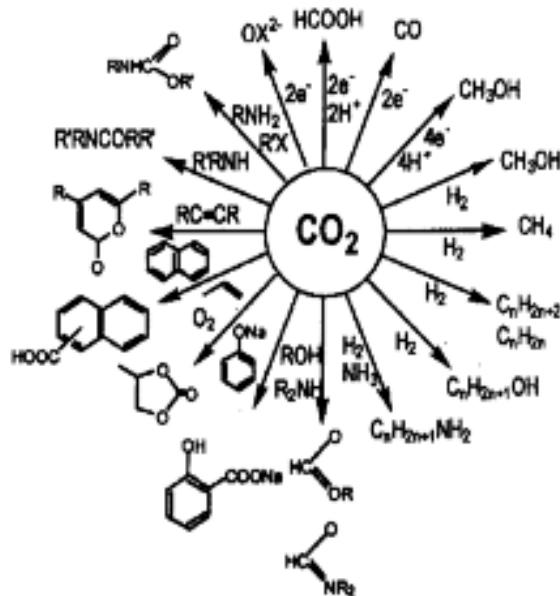
(Million Metric Tons Carbon Equivalent Per Year)

CO <sub>2</sub> emissions and utilization	Reference
Total CO <sub>2</sub> added to atmosphere	IPCC (1995)
Burning fossil fuels	5,500
Deforestation	1,600
Total worldwide CO <sub>2</sub> 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 <sub>2</sub> 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 <sub>2</sub> emission	3%
Agricultural chemical complex in the lower Mississippi River corridor excess high purity CO <sub>2</sub>	Hertwig et al. (2002)
0.183	
CO <sub>2</sub> used in chemical synthesis	Arakawa et al. (2001)
30	

This table gives a summary 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<sub>2</sub> per year are used for chemical synthesis. However, there is excess of high purity CO<sub>2</sub> that is discharged to the atmosphere, mainly from ammonia plants.

# 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-: Carbamio esters
  - NCO: Isocyanates
  - N-C(O)-N: Ureas
- Use as a solvent
- Energy rich products  
CO, CH<sub>3</sub>OH



From Creutz and Fujita, 2000

There have been several conferences in the past ten years on carbon dioxide reactions that consider using it as a raw material. This diagram 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.

Currently, 110 million metric tons per year of CO<sub>2</sub> are used in chemical synthesis as shown on the next slide.

## Commercial Uses of CO<sub>2</sub>

- 110 million tons of CO<sub>2</sub> for chemical synthesis
  - Urea (chiefly, 90 million ton of CO<sub>2</sub>)
  - Methanol (1.7 million tons of CO<sub>2</sub>)
  - Polycarbonates
  - Cyclic carbonates
  - Salicylic acid
  - Metal carbonates

This information from an NRC report shows the commercial chemical uses of CO<sub>2</sub>. The largest use is for urea production that reached about 90 million metric tons per year in 1997 according to the report. Other commercially important products are methanol and polycarbonates.

### Principle Organic Uses

- Urea  $\text{CO}_2 + 2\text{NH}_3 \rightarrow \text{CO}(\text{NH}_2)_2 + \text{H}_2\text{O}$
- Methanol: CO<sub>2</sub> is used to balance the CO : H<sub>2</sub> ratio and to control the heat of the CO hydrogenation.
- Polycarbonates
- Cyclic carbonates  $\text{CO}_2 + \text{RCHCH}_2 + 0.5\text{O}_2 \rightarrow \text{RCHCH}_2\text{OC(O)O}$
- Salicylic acid (Aspirin)  $\text{CO}_2 + \text{C}_6\text{H}_5\text{ONa} \rightarrow \text{C}_6\text{H}_4(\text{COOH})\text{OH}$

Catalytic Reactions of CO <sub>2</sub> from Various Sources			
<b>Hydrogenation</b>		<b>Hydrolysis and Photocatalytic Reduction</b>	
CO <sub>2</sub> + 3H <sub>2</sub> → CH <sub>3</sub> OH + H <sub>2</sub> O	methanol	CO <sub>2</sub> + 2H <sub>2</sub> O → CH <sub>3</sub> OH + O <sub>2</sub>	
2CO <sub>2</sub> + 6H <sub>2</sub> → C <sub>2</sub> H <sub>5</sub> OH + 3H <sub>2</sub> O	ethanol	CO <sub>2</sub> + H <sub>2</sub> O → HC=O-OH + 1/2O <sub>2</sub>	
CO <sub>2</sub> + H <sub>2</sub> → CH <sub>3</sub> -O-CH <sub>3</sub>	dimethyl ether	CO <sub>2</sub> + 2H <sub>2</sub> O → CH <sub>4</sub> + 2O <sub>2</sub>	
<b>Hydrocarbon Synthesis</b>			
CO <sub>2</sub> + 4H <sub>2</sub> → CH <sub>4</sub> + 2H <sub>2</sub> O	methane and higher HC		
2CO <sub>2</sub> + 6H <sub>2</sub> → C <sub>2</sub> H <sub>4</sub> + 4H <sub>2</sub> O	ethylene and higher olefins		
<b>Carboxylic Acid Synthesis</b>			
CO <sub>2</sub> + H <sub>2</sub> → HC=O-OH	formic acid	CO <sub>2</sub> + ethylbenzene → styrene	
CO <sub>2</sub> + CH <sub>4</sub> → CH <sub>3</sub> -C=O-OH	acetic acid	CO <sub>2</sub> + C <sub>3</sub> H <sub>8</sub> → C <sub>3</sub> H <sub>6</sub> + H <sub>2</sub> + CO dehydrogenation of propane	
		CO <sub>2</sub> + CH <sub>4</sub> → 2CO + H <sub>2</sub> reforming	
<b>Graphite Synthesis</b>			
CO <sub>2</sub> + H <sub>2</sub> → C + H <sub>2</sub> O	CH <sub>4</sub> → C + H <sub>2</sub>		
	CO <sub>2</sub> + 4H <sub>2</sub> → CH <sub>4</sub> + 2H <sub>2</sub> O		
<b>Amine Synthesis</b>			
CO <sub>2</sub> + 3H <sub>2</sub> + NH <sub>3</sub> → CH <sub>3</sub> -NH <sub>2</sub> + 2H <sub>2</sub> O	methyl amine and higher amines		

This information categorizes the carbon dioxide reactions that produce 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.

An important reaction that is included in this evaluation using the System is the direct catalytic reaction of carbon dioxide and methane to produce acetic acid.

## Methanol Commercial Production

- Catalytic methanol production from CO and H<sub>2</sub>. Liquid-entrained micro-sized copper-based catalysts, 5-8 MPa and 250-260°C, bed-in-place or multi-tray reactor.
  - steam reforming: CH<sub>4</sub> + H<sub>2</sub>O = CO + 3H<sub>2</sub>
  - water-gas shift reaction: CO<sub>2</sub> + H<sub>2</sub> = CO + H<sub>2</sub>O
  - catalytic synthesis: CO + 2H<sub>2</sub> = CH<sub>3</sub>OH

This is the commercial production of methanol from methane, steam and carbon dioxide. There are three steps in this process. The third step is methanol produced from CO and H<sub>2</sub>.

## Methanol from CO<sub>2</sub>

- Raney Cu-Zr catalyst, flow reactor, 523 K, 5 MPa, CO<sub>2</sub>/H<sub>2</sub> = 1/3, SV=18000h<sup>-1</sup>, methanol activity 941 mg-MeOH/ml-cat·h, (p.267).
- Pd promoted Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts, internal recycle reactor (300 cm<sup>3</sup> volume, 100 cm<sup>3</sup> catalyst basket), 5 MPa, 250°C, H<sub>2</sub>/CO<sub>2</sub>=4/1, flowrate is larger than 240 ml/min (s.t.p.), methanol selectivity about 58-65% (p.351).
- Production capacity 50 kg/day, multicomponent catalyst Cu/ZnO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/Ga<sub>2</sub>O<sub>3</sub>, tube reactor, 523K, 5 MPa, H<sub>2</sub>/CO<sub>2</sub>=3/1, SV=10,000h<sup>-1</sup>, high selectivity with the purity of methanol 99.9%, methanol production rate 600 g/l-cat·h (p. 357).

Source: Advances in Chemical Conversions for Mitigating Carbon Dioxide, Proceedings of the Fourth International Conference on Carbon Dioxide Utilization, Kyoto, Japan, September 7-11, 1997

The next two slides are about the new/experimental methods to produce methanol from CO<sub>2</sub>. All of this information is from the source. There are about 11 new methods to produce methanol and here only 6 are listed as examples.

The purpose is to emphasize the opportunities and the importance of CO<sub>2</sub> reuse for chemical synthesis, especially for methanol production. Research results like the ones shown here illustrate the potential for new, energy efficient plants that use CO<sub>2</sub> as a raw material.

## Methanol from CO<sub>2</sub> (Cont'd)

- Ru promoted Cu-based catalysts (CuO-ZnO/TiO<sub>2</sub>), conventional continuous flow reactor, 1.0MPa, 553 K, molar ratio H<sub>2</sub>/CO<sub>2</sub>=4/1, W/F<sub>CO<sub>2</sub>,0</sub> =570 kg-cat·s/mol, 7.7% conversion, 20.4% selectivity (p.427).
- Hybrid catalyst of Cu/ZnO/Cr<sub>2</sub>O<sub>3</sub> and CuNaY zeolite, fixed bed micro-reactor, 523K, 30 kg/cm<sup>2</sup>, H<sub>2</sub>/CO<sub>2</sub> =3/1, flow rate=30 ml/min, conversion to methanol and dimethyl ether (oxygenates)= 9.37%, dimethyl ether selectivity in oxygenates=36.7% (p.447).
- Cu/ZnO-based multicomponent catalyst (Cu/ZnO/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>) modified with the special silicone oil (5wt%), liquid-phase continuous reactor, 523K, 15MPa, H<sub>2</sub>/CO<sub>2</sub>=3/1, recycle rate of solvent =100 l-solvent/l-cat/hr, 650 g-MeOH/kg-cat/hr (p. 521).

Source: Advances in Chemical Conversions for Mitigating Carbon Dioxide, Proceedings of the Fourth International Conference on Carbon Dioxide Utilization, Kyoto, Japan, September 7-11, 1997

Details of the methods to determine new processes to produce methanol from this new information will be discussed later.

The methods to determine a new process to produce methanol from this information are as followed:

1. Simulate process using HYSYS.
2. Estimate utilities required.
3. Perform economic analysis.
4. Obtain process constraint equations from HYSYS simulation.
5. Maximize the profit function to find the optimum process configuration with the System.
6. Incorporate into superstructure.

All of these steps will be discussed in detail later.

## Comparison of Power Generation

	Conventional	Cogeneration
Operating efficiency	33%	77%
Heat rate (BTU/kWh)	>10,000	5,000-6,000
NO <sub>x</sub> emission (lbs of NO <sub>x</sub> / MWh)	4.9	0.167
CO <sub>2</sub> emission (tons of CO <sub>2</sub> / MWh)	1.06	0.30

In cogeneration or combined heat and power, CHP, a combustion turbine, CT, generates power, and the turbine exhaust is used to produce steam in a heat recovery steam generator, HSRG. The operating efficiency of a CHP utility plant is 77%, and the average operating efficiency of existing power plants is 33% conversion of energy to electricity. Most CHP applications at large industrial facilities, operate at between 5,000 to 6,000 BTUs of energy per kWh. Traditional power plants operate at heat rates over 10,000 BTUs of energy per kWh.

A five MW combustion turbine produces 0.167 lbs of NOx per MWH. The average utility power plant emits approximately 4.9 lbs of NOx for every megawatt hour (MWH). A five MW gas turbine emits about 0.30 tons of CO<sub>2</sub> per MWH, and an average utility plant produces about 1.06 tons of CO<sub>2</sub> per MWH.

## Related Work and Programs

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

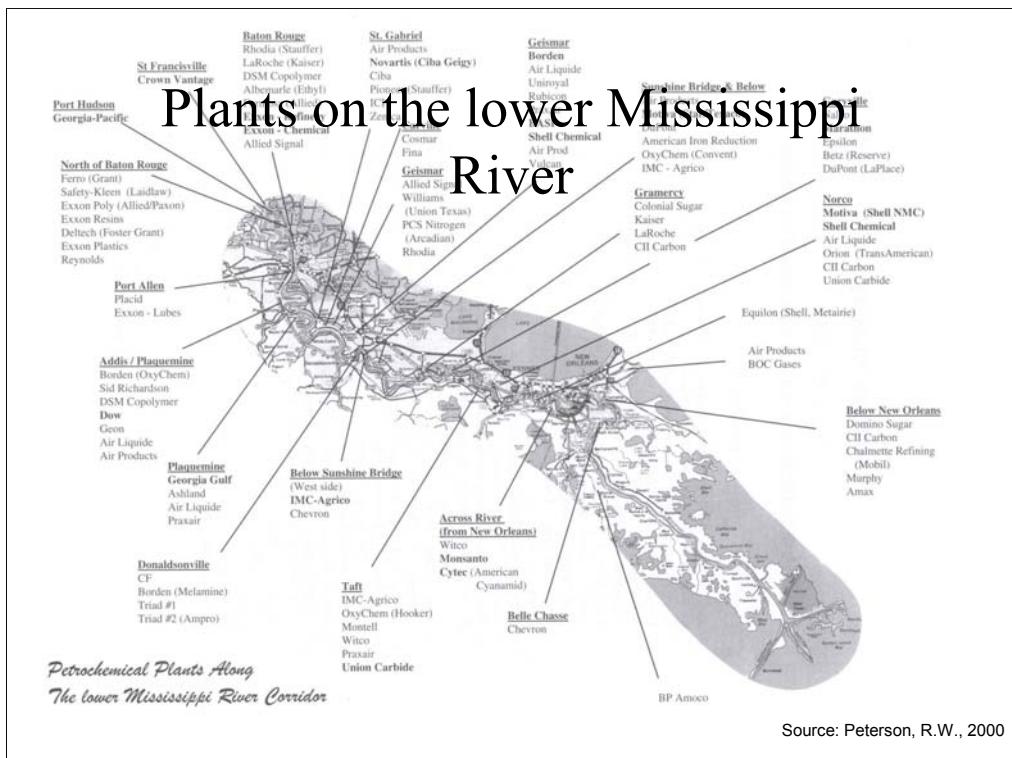
Aspen Technology is a leading modeling technology company, and they have programs for plant design, supply chains and manufacturing. These programs are licensed to a company for a specific application. However, they do not have an application similar the Chemical Complex and Cogeneration Analysis System described here.

The web sites of the two Federal agencies have programs that help analyze plants or parts of plants but not multi-plant production complexes.

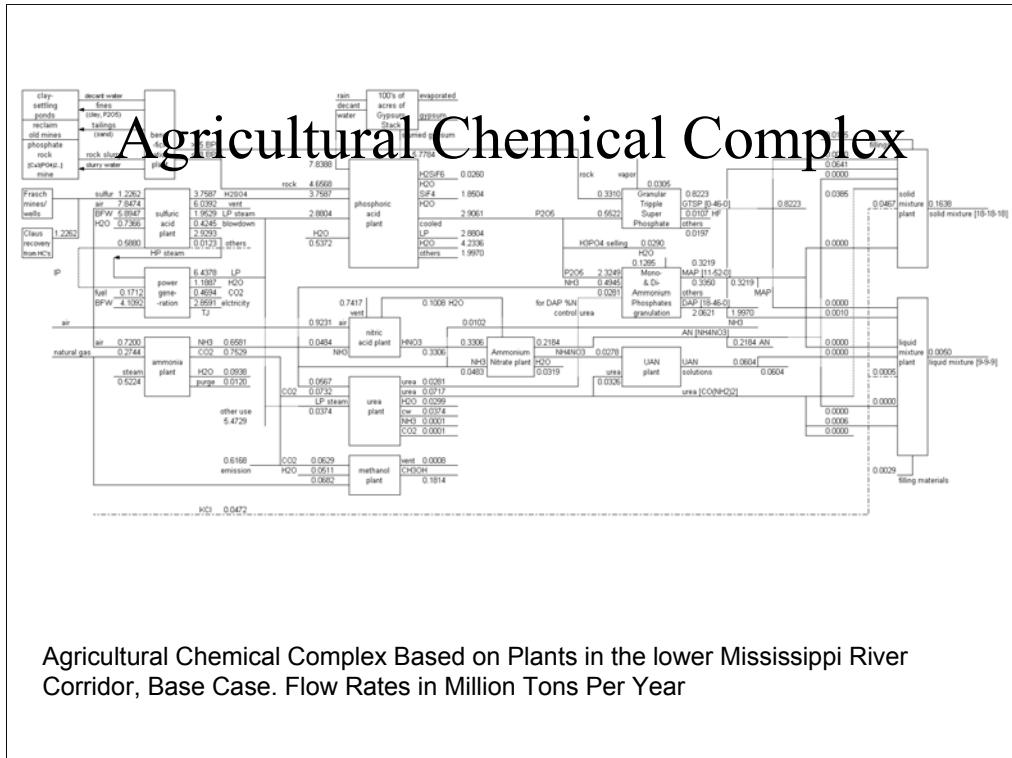
## Chemical Complexes in the World

Continent	Name and Site	Notes
North America	<ul style="list-style-type: none"> <li>•Gulf coast petrochemical complex in Houston area (U.S.A.) and</li> <li>•Chemical complex in the Baton Rouge-New Orleans Mississippi River Corridor (U.S.A.)</li> </ul>	<ul style="list-style-type: none"> <li>•Largest petrochemical complex in the world, supplying nearly two-thirds of the nation's petrochemical needs</li> </ul>
South America	<ul style="list-style-type: none"> <li>•Petrochemical district of Camacari-Bahia (Brazil)</li> <li>•Petrochemical complex in Bahia Blanca (Argentina)</li> </ul>	<ul style="list-style-type: none"> <li>•Largest petrochemical complex in the southern hemisphere</li> </ul>
Europe	<ul style="list-style-type: none"> <li>•Antwerp port area (Belgium)</li> <li>•BASF in Ludwigshafen (Germany)</li> </ul>	<ul style="list-style-type: none"> <li>•Largest petrochemical complex in Europe and world wide second only to Houston, Texas</li> <li>•Europe's largest chemical factory complex</li> </ul>
Asia	<ul style="list-style-type: none"> <li>•The Singapore petrochemical complex in Jurong Island (Singapore)</li> <li>•Petrochemical complex of Daqing Oilfield Company Limited (China)</li> <li>•SINOPEC Shanghai Petrochemical Co. Ltd. (China)</li> <li>•Joint-venture of SINOPEC and BP in Shanghai under construction (2005) (China)</li> <li>•Jamnagar refinery and petrochemical complex (India)</li> <li>•Sabic company based in Jubail Industrial City (Saudi Arabia)</li> <li>•Petrochemical complex in Yanbu (Saudi Arabia)</li> <li>•Equate (Kuwait)</li> </ul>	<ul style="list-style-type: none"> <li>•World's third largest oil refinery center</li> <li>•Largest petrochemical complex in Asia</li> <li>•World's largest polyethylene manufacturing site</li> <li>•World's largest &amp; most modern for producing ethylene glycol and polyethylene</li> </ul>
Oceania	<ul style="list-style-type: none"> <li>•Petrochemical complex at Altona (Australia)</li> <li>•Petrochemical complex at Botany (Australia)</li> </ul>	
Africa	petrochemical industries complex at Ras El Anouf (Libya)	one of the largest oil complexes in Africa

This information describes many of the chemical complexes worldwide. The System could be applied to these complexes, also.



This map shows the location of plants in the lower Mississippi River corridor. There are about 150 plants that consume 1.0 quad ( $10^{15}$  Btu/yr) of energy and generate about 215 million pounds per year of pollutants. Diagram is from R. W. Peterson "Giants on the River" Homesite Company, Baton Rouge (1999).



This diagram shows the plants and their interconnections in the agricultural chemical complex. The blocks represent multiple plants. The sulfuric acid block has five plants owned by two companies. There are ten production units plus associated utilities for power, steam and cooling water and facilities for waste treatment.

The raw materials used in the agricultural chemical complex include air, water, natural gas, sulfur, phosphate rock and potassium chloride as shown on the above figure. The products are a typical solid blend of [18% N-18% P2O5-18% K2O], a liquid blend of [9-9-9], mono- and di-ammonium phosphate (MAP and DAP), granular triple super phosphate (GTSP), urea, ammonium nitrate, and urea ammonium nitrate solution (UAN), phosphoric acid, ammonia and methanol. The flow rates shown on the diagram are in million tons per year. Intermediates are sulfuric acid, phosphoric acid, ammonia, nitric acid, urea and carbon dioxide. The intermediates are used to produce MAP and DAP, GTSP, urea, ammonium nitrate, and UAN. Also, potassium supplied as potassium chloride for blends is not produced on the Gulf coast but is imported from New Mexico and Utah, among other states. Ammonia is used in direct application to crops and other uses. MAP, DAP, UAN and GTSP are also used in direct application to crops. Phosphoric acid can be used in other industrial applications. Methanol is used to produce formaldehyde, methyl esters, amines and solvents, among others, and is included for its use of ammonia plant byproduct - carbon dioxide.

# 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

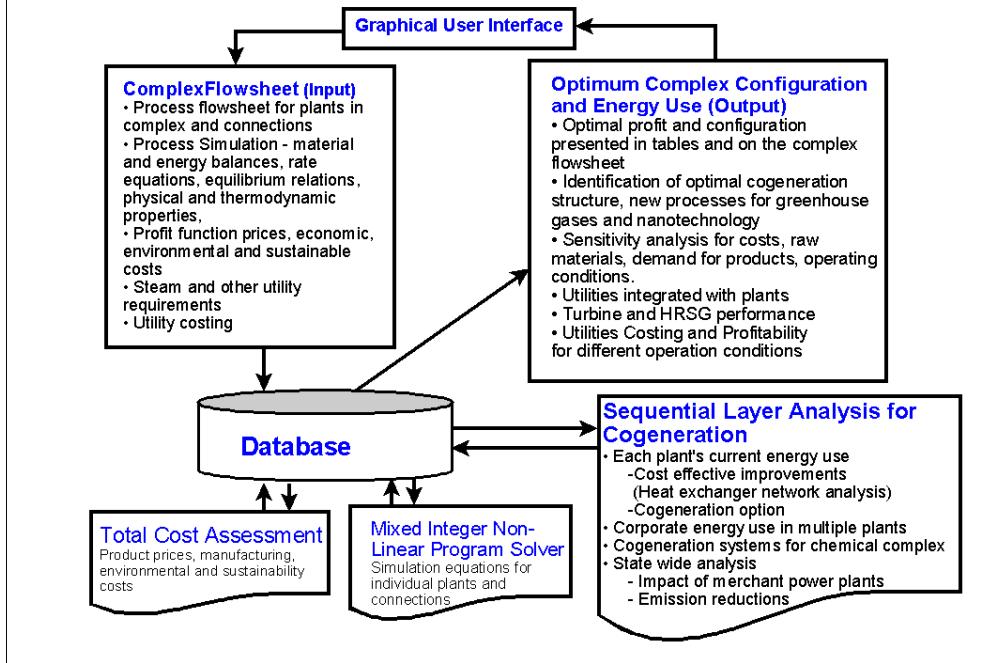
Determines the best energy use based on economics, energy efficiency, regulatory emissions and environmental impacts from greenhouse gas emissions.

The System combines the two analyses shown here.

One determines the optimum configuration of plants from a superstructure. The other uses cogeneration for best energy use.

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

# Structure of the System



This diagram shows the structure of the System. The complex flow sheet is drawn, and material and energy balances, rate equations and equilibrium relations for the plants are entered through windows as equality constraints using the format of the GAMS programming language that is similar to Excel and stored in an Access database. Process unit capacities, availability of raw materials and demand for product are entered as inequality constraints and stored in the database. The economics are entered through the friendly graphical user interface. The input includes incorporating new plants that use greenhouse gases as raw materials in the existing complex of plants

The System takes the equations in the database and writes and runs a GAMS program to solve the mixed integer nonlinear programming problem for the optimum configuration of the complex. Then the important information from the GAMS solution is presented to the user on the flow diagram, on the cogeneration diagram and in summary tables. The results can be exported to Excel, if desired.

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 integrated cogeneration sequential layer analysis determines cost effective improvements for individual plants using heat exchanger network analysis and cogeneration opportunities. Then these results are used to determine the optimum complex configuration and utilities integrated with the plants.

## AIChE Total Cost Assessment

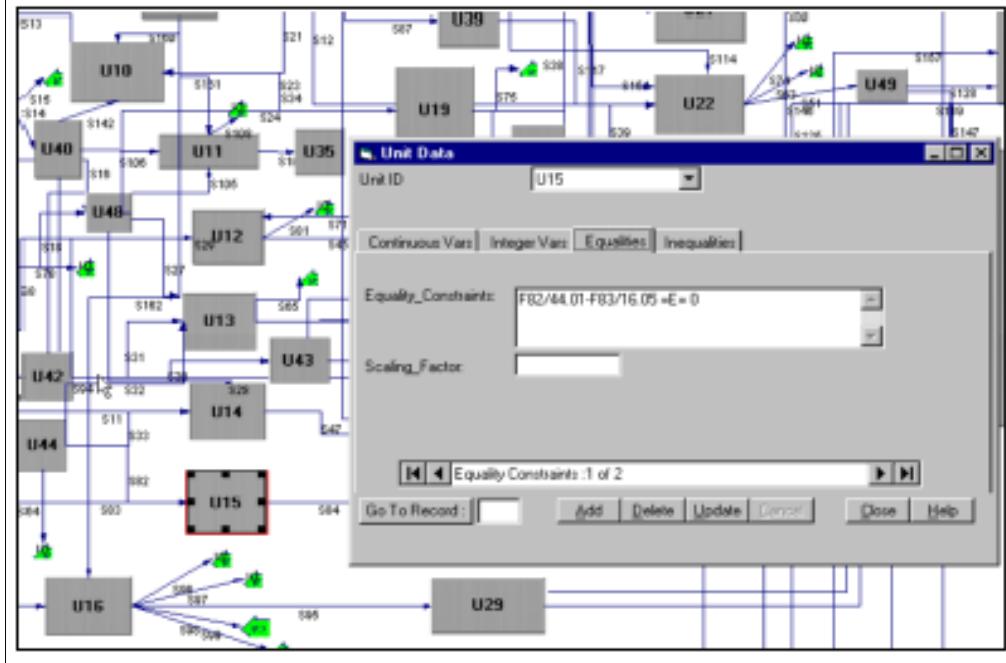
- Includes five types of costs: I direct, II overhead, III liability, IV internal intangible, V external (borne by society - sustainable)
- Sustainable costs are costs to society from damage to the environment caused by emissions within regulations, e.g., sulfur dioxide 4.0 lb per ton of sulfuric acid 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

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.

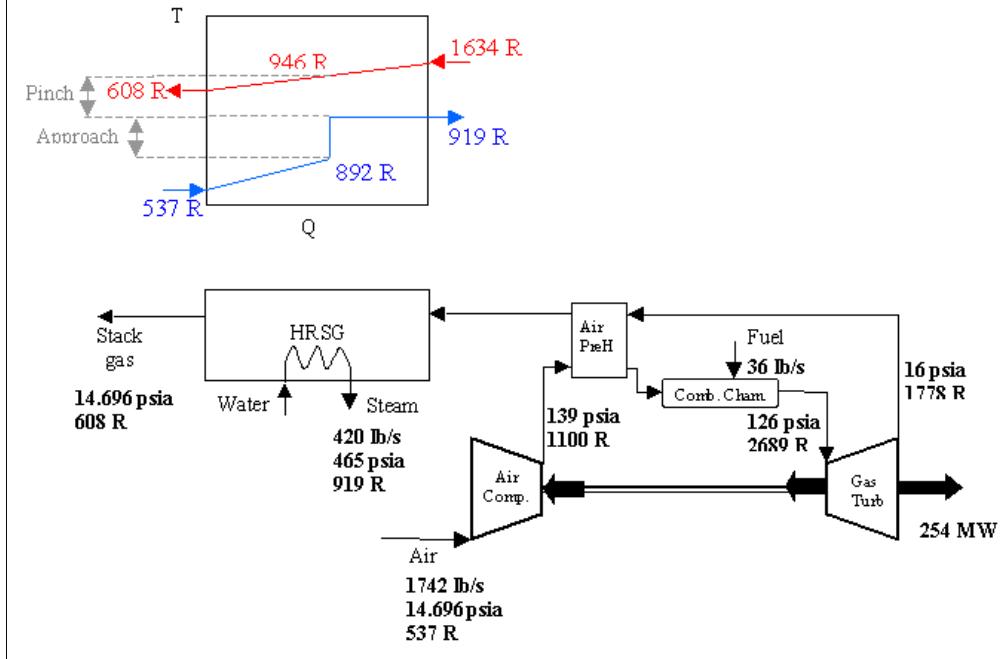
### Illustration of Input to the System for Unit Data



This slide shows a screen print of the window that is used to enter a plant model. Here a material balance equation has been entered as an equality constraint. The diagram in the background is the process flow diagram of the agricultural chemical complex. All interactions with the System are through a graphical user interface written in Visual Basic.

Features for developing flow sheets include adding, changing and deleting the equations that describe units and streams and their properties. Usual Windows features also can be used, including cut, copy, paste, delete, print, zoom, reload, update and grid, among others.

## Typical Cogeneration Results on the CHP Diagram



This slide shows a screen print of the window that gives the results from the cogeneration analysis.

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

- Base cases
- Superstructures
- Optimal structures

There are two base cases. First, the base case of existing plants is described as Base Case 1. Then this base case (Base Case 2) is expanded to include an acetic acid plant.

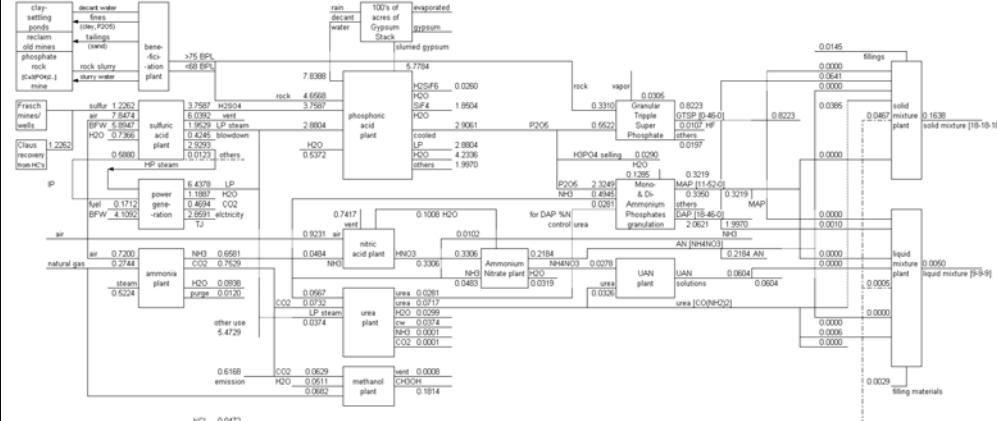
Base Case 1 is extended into Superstructure 1 and Base Case 2 is extended into Superstructure 2. Then the optimal structures obtained from the superstructures by solving a mixed integer nonlinear programming problem.

In summary, there are two base cases, two superstructures and two optimal structures.



This is a map of the plants in the region. We have selected plants that are associated with producing agricultural chemicals.

## Agricultural Chemical Complex Based on Plants in the Lower Mississippi River Corridor, Base Case. Flow Rates in Million Tons Per Year



This is the diagram of the plants in the agricultural chemical complex, called Base Case 1 of existing plants. 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 more than one plant owned by two companies.

For this base case there were 328 equality constraint equations describing the material and energy balances and chemical conversions. Also, there were 21 inequality constraint equations describing the demand for product, availability of raw materials and range on the capacities of the individual plants in the complex.

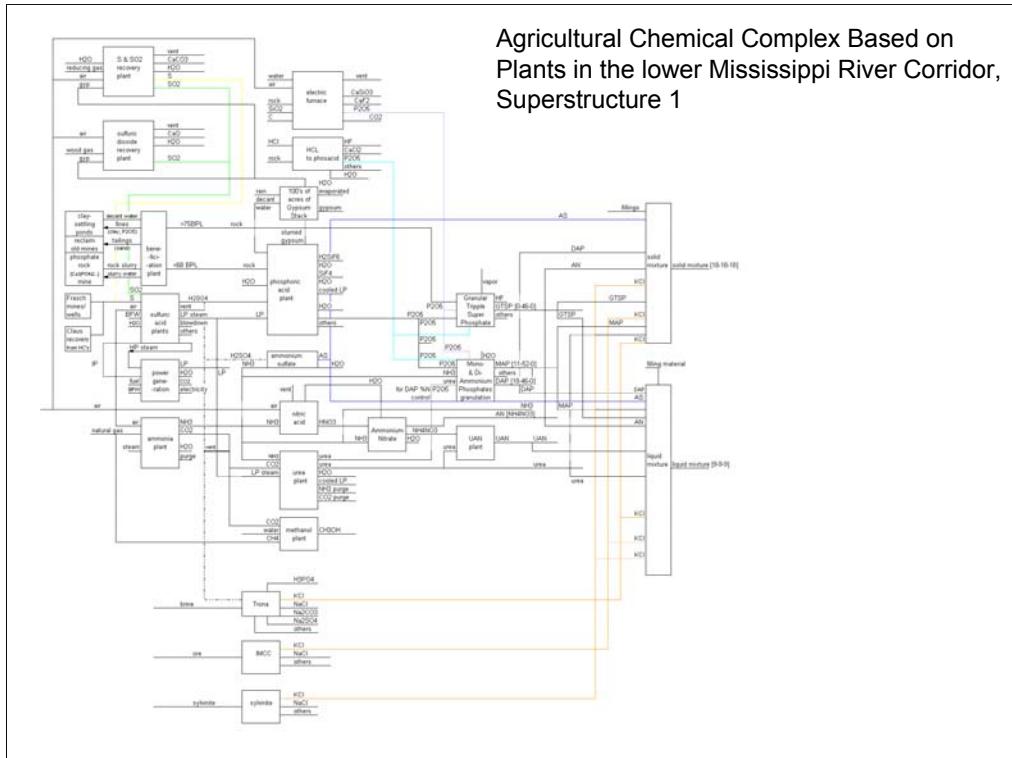
# Agricultural Chemical Complex

Processes in Superstructure 1	
Processes in Base Case 1	
Ammonia	Electric furnace process for phosphoric acid
Nitric acid	HCl process for phosphoric acid
Ammonium nitrate	Trona process for KCl
Urea	IMCC process for KCl
UAN	Ammonium sulfate
Methanol	SO <sub>2</sub> recovery from gypsum process
Granular triple super phosphate	S & SO <sub>2</sub> recovery from gypsum process
MAP & DAP	
Power generation	
Solid blend	
Liquid blend	
Contact process for Sulfuric acid	
Wet process for phosphoric acid	
Sylvinitic process for KCl	

First Base Case 1 and Superstructure 1 are described and Optimal Structure 1 was obtained from Superstructure 1.

This table is a convenient way to show the plants in Base Case 1 and the plants added in Superstructure 1. Superstructure 1 additionally includes electric furnace and HCl processes for phosphoric acid, Trona and IMCC processes for KCl, ammonium sulfate, and the S and SO<sub>2</sub> recovery from gypsum processes.

Note: The base case and superstructure produce same final products but the superstructure has more alternative ways to produce the chemicals.



This diagram shows Superstructure 1 that was developed by adding alternative processes that gave additional options for manufacturing products from the complex based on Base Case 1. These alternative plants are summarized on the next slide.

# Superstructure Characteristics

## Options

- Three options for producing phosphoric acid
- Three options for producing potassium chloride
- One option for sulfuric acid
- Two options for recover sulfur and sulfur dioxide
- New plants for
  - ammonium sulfate
  - recover sulfur and sulfur dioxide

## Mixed Integer Nonlinear Program

- 659 continuous variables
- 8 integer variables
- 542 equality constraint equations
  - for material and energy balances
- 31 inequality constraints for availability of raw materials
  - demand for product, capacities of the plants in the complex

This slide summarizes the options incorporated in Superstructure 1. Also, it give the size of the mixed integer nonlinear programming problem.

The superstructure included three options for producing phosphoric acid and potassium chloride. There are one option for sulfuric acid production. There are new plants to produce ammonium sulfate and to recover sulfur and sulfur dioxide.

The model of the superstructure has 659 continuous variables, 8 integer variables, 542 equality constraint equations for material and energy balances and 31 inequality constraints for availability of raw materials, demand for product and capacities of the plants in the complex.

## Raw Material and Product Prices

Raw Materials	Cost ( \$/T)	Raw Materials	Cost ( \$/T)	Products Price(\$/T)
Natural Gas	40	Market cost		Ammonia 190
Phosphate Rock		for short term		Methanol 96
wet process	27	purchase		Acetic Acid 623
electrofurnace	24	Reducing gas	1394	Solid Blend 160
HCl process	25	Wood gas	634	Liquid Blend 60
GTSP process	30			GTSP 142
		<u>Sustainable Costs and Credits</u>		MAP 180
		Credit for CO <sub>2</sub>	6.50	DAP 165
HCl	50	Consumption		NH <sub>4</sub> NO <sub>3</sub> 153
Sulfur		Debit for CO <sub>2</sub>	3.25	UAN 112
Frasch	42	Production		Urea 154
Claus	38	Credit for HP Steam	10	H <sub>3</sub> PO <sub>4</sub> 320
Brine KCl ore	2	Credit for IP Steam	6.4	
Searles Lake KCl ore	15	Credit for gypsum	5	
Sylvinit KCl ore	45	Consumption		
C electrofurnace	760	Debit for gypsum	2.5	
KCl	107	Production		
H <sub>3</sub> PO <sub>4</sub>	352	Debit for NO <sub>x</sub>	1025	
H <sub>2</sub> SO <sub>4</sub>	86	Production		

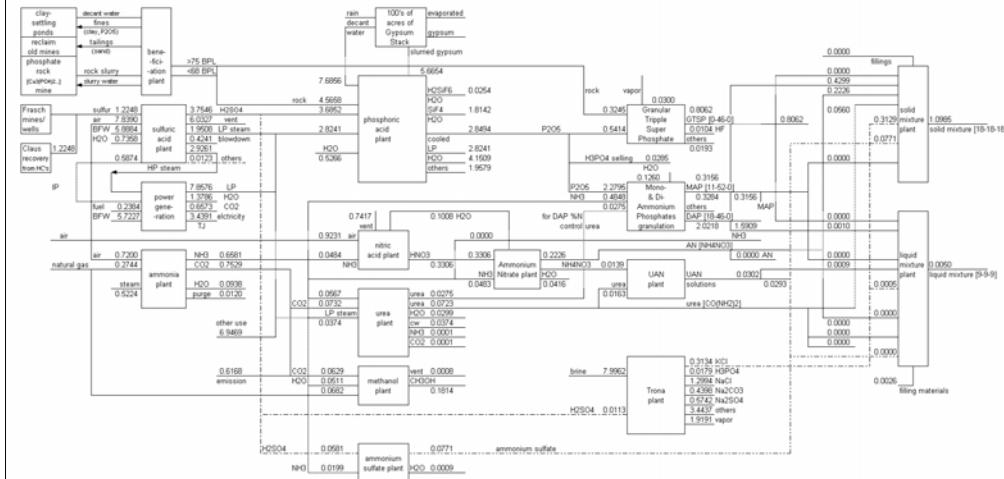
Source Green Market Sheet (July 10, 2000), Internet and AIChE/CWTR TCA Report.

This table gives the sale prices for products and costs of raw material which were used in the economic model of the complex. Also shown are sustainable costs and credits.

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. These costs are arbitrary but a conservative approach. Emissions trading costs of carbon dioxide is about \$50.00 per ton.

## Optimal Structure 1 for Agricultural Chemical Complex (Flow Rates in Million Tons Per Year)



This slide gives the diagram of the optimal configuration of plants obtained from Superstructure 1. The ammonium sulfate is operated. Sylvite process was replaced by Trona process for KCl production. The next slide gives a summary of the results.

Comparison of Base Case 1 and Optimal Structure 1

Plant name	Base case 1		Optimal structure 1		
	Capacity (t/year) (upper-lower bounds)	Capacity (t/year)	Requirement (TJ/year)	Capacity (t/year)	Requirement (TJ/year)
Ammonia	329,030-658,061	658,061	3,820	658,061	3,820
Nitric acid	0-178,547	178,525	656	178,525	656
Ammonium nitrate	113,398-226,796	226,796	125	226,796	156
Urea	49,695-99,790	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	30,240	0
MAP	0-321,920	321,912		315,620	
DAP	0-2,062,100	2,062,100	2,137	2,021,801	2,095
GTSP	0-822,300	822,284	1,036	806,214	1,016
Contact process sulfuric acid	1,851,186-3,702,372	3,702,297	-14,963	3,698,313	-14,946
Wet process phosphoric acid	697,489-1,394,978	1,394,950	7,404	1,367,689	7,259
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
Ammonium sulfate	0-2,839,000	na	na	77,139	44
Trona process for KCl	0-5,600,000	na	na	313,453	4,582
IMCC process for KCl	0-5,600,000	na	na	0	0
Sylvinitic process for KCl	0-5,600,000	47,159	895	0	0
Solid mixture	5,000 lower bound	163,859	0	1,098,536	0
Liquid mixture	5,000 lower bound	5,000	0	5,000	0
SO <sub>2</sub> recovery from gypsum	0-1,804,417	na	na	0	0
S & SO <sub>2</sub> recovery from gypsum	0-903,053	na	na	0	0
Ammonia sale		10,227		0	
Ammonium Nitrate sale		218,441		0	
Urea sale		0		0	
UAN sale		60,480		29,327	
MAP sale		321,912		315,620	
DAP sale		1,997,003		1,590,961	
GTSP sale		822,284		806,214	
Wet process phosphoric acid sale		13,950		13,677	
Methanol sale		181,437		181,437	
Total energy requirement			2,092		5,663

Production rates for the products in the optimal solution were constrained by their capacity limit, which were set at Base Case 1 values. In addition, it was optimal to obtain KCl from the Trona process. It was optimal to operate the ammonium sulfate plant. Meanwhile, the energy requirement of ammonium nitrate plant in optimal structure was different from base case with 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 profit which includes the economic, environmental and sustainable costs increased about 8.58% from Base Case 1 to the optimal solution, also environmental cost increased about 5.24%, and sustainable costs increased about 2.18%. Also the energy requirements increased from 2092 to 5663 TJ/yr. The sylvinitic plant (0.019 TJ/t) consuming more energy in Base Case 1 was replaced by the Trona plant (0.015TJ/t) in the optimal solution to reduce energy consumption. The system can select plants for the complex with less energy consumption.

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.

## Comparison of Acetic Acid Processes

Process	Conventional Process	New Catalytic Process
Raw Materials	Methanol, Carbon Monoxide	Methane, Carbon Dioxide
Reaction Condition	450K, 30bar	350K, 25bar
Conversion of methane	100%	97%
Equipment	reactor, flash drum, four distillation columns	reactor, distillation column

This gives a comparison of the conventional process for acetic acid and catalytic processes using carbon dioxide as a raw material. The difference is in the utility requirements. In the conventional process, 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 methane in excess carbon dioxide. 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 (Moulijn, , et al., 2001). This process includes a reactor, a flash drum and four distillation columns. The new process requires a catalytic reactor operating at 350 K and 25 bar for a 97% conversion of methane in excess carbon dioxide, and equipment includes a reactor and a distillation column to separate the unreacted carbon dioxide for recycle and acetic acid product.

# Production Costs for Acetic Acid

Moulijn, et al., 2001

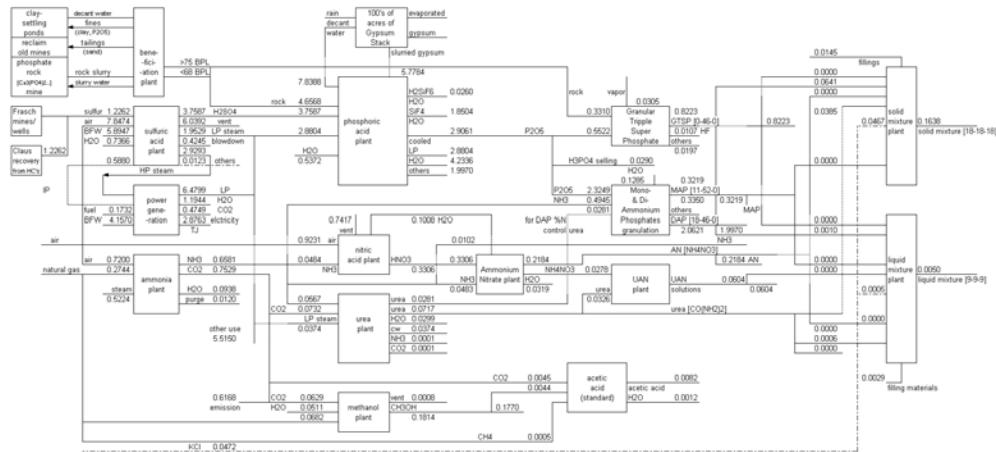
Plant Production Cost, (cents per kg)	Methanol Carbon Monoxide	Methane Carbon Dioxide
Raw materials	21.6	21.6
Utilities	3.3	1.7
Labor	1.2	1.2
Other (capital, catalyst)	10.1	10.1
Total Production Cost	36.2	34.6

Current market price 79 cents per kg

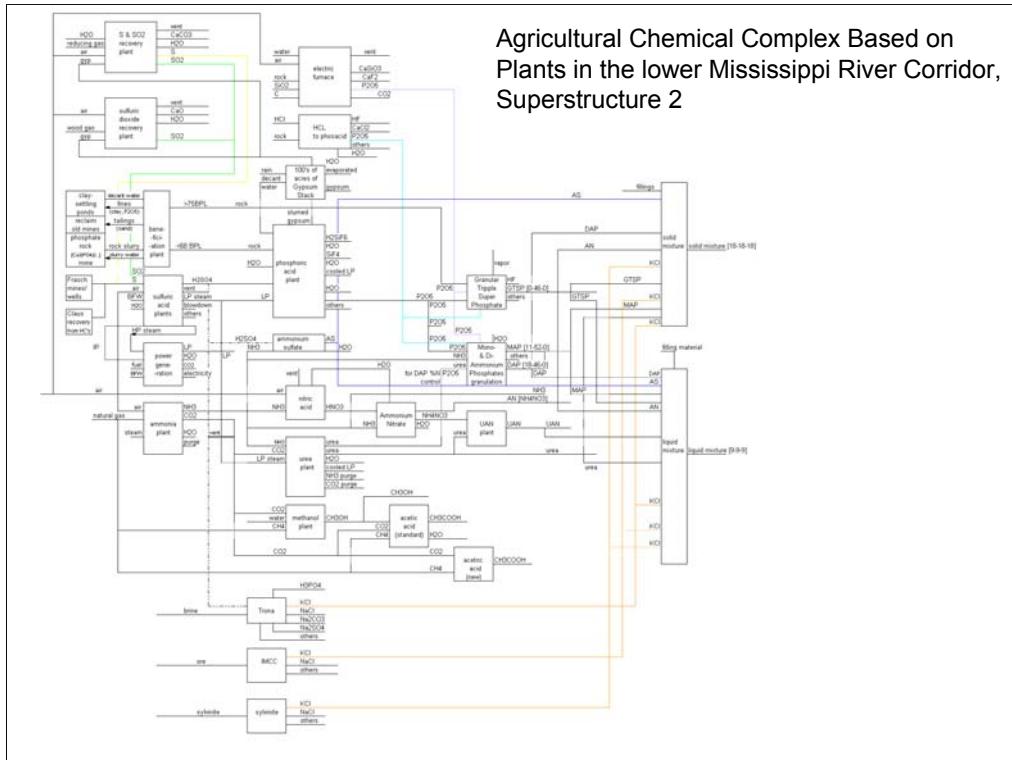
This slide gives the economics for the two processes that was included in the System. For a conservative estimate, the economic, energy and environmental benefits were evaluated on the savings associated with the acetic acid water separation which is not required in the new plant. In the above Table the production costs are itemized from Moulijn, 2001, and the raw material, labor and capital cost should be comparable for the conventional (methanol carbon monoxide) and new (methane carbon dioxide) plants if not less for the new plant. A typical 100 million pound per year plant was used as a basis.

There are eleven companies producing acetic acid in North America with plants of capacities from 44 to 2,000 million pounds per year with a total capacity of 5,544 million pounds per year, and demand is growing at 3% per year (ChemExpo Chemical Profile Acetic Acid, 1998).

**Agricultural Chemical Complex Based on Plants in the Lower Mississippi River Corridor, Intermediate Case. Flow Rates in Million Tons Per Year**



This diagram shows Base Case 2 where a standard acetic acid plant with methanol as feedstock was added to Base Case 1. This is the first step to extend the agricultural chemical complex into the petrochemical complex focusing on the CO<sub>2</sub> reuse.



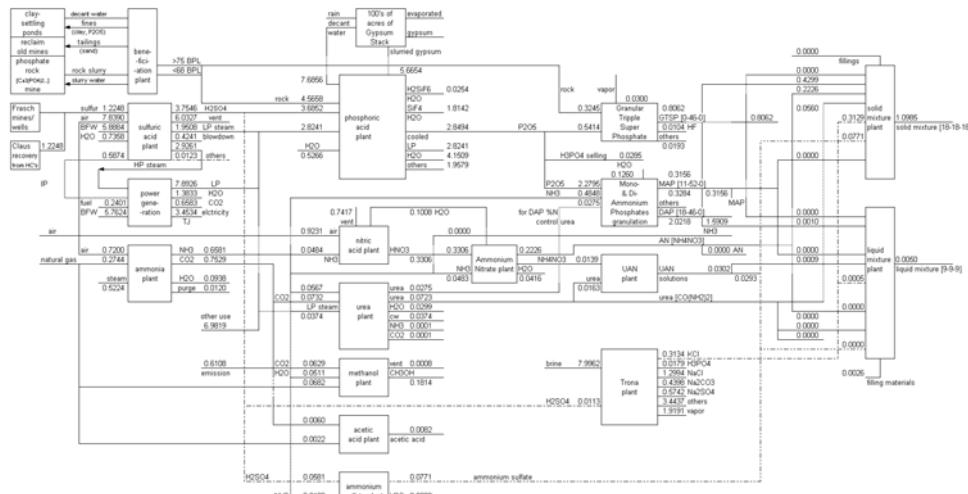
This diagram shows Superstructure 2 that was developed by adding alternative processes that gave additional options for manufacturing products from the complex based on Base Case 2. These alternative plants are summarized on the next slide.

## Agricultural Chemical Complex

Processes in Superstructure 2	
Processes in Base Case 2	
	Electric furnace process for phosphoric acid
Ammonia	HCl process for phosphoric acid
Nitric acid	Trona process for KCl
Ammonium nitrate	IMCC process for KCl
Urea	Ammonium sulfate
UAN	SO <sub>2</sub> recovery from gypsum process
Methanol	S & SO <sub>2</sub> recovery from gypsum process
Granular triple super phosphate	Acetic acid –new method
MAP & DAP	
Power generation	
Solid blend	
Liquid blend	
Contact process for Sulfuric acid	
Wet process for phosphoric acid	
Sylvinitic process for KCl	
Acetic acid-standard method	

The only difference between Base Case 1 and Base Case 2 is an existing acetic acid plant was added in Base Case 2. This is the first step from expanding the agricultural chemical complex to a petrochemical complex.

## Optimal Structure 2 for Agricultural Chemical Complex (Flow Rates in Million Tons Per Year)



This slide gives the diagram of the optimal configuration of plants obtained from Superstructure 2. The ammonium sulfate and catalytic process for acetic acid are operated. The next slide gives a summary of the results.

Comparison of Base Case 2 and Optimal Structure 2

		Base case 2	Optimal structure 2		
Plant name	Capacity (t/year) (upper-lower bounds)	Capacity (t/year)	Requirement (TJ/year)	Capacity (t/year)	Requirement (TJ/year)
Ammonia	329,030-688,061	658,061	3,820	658,061	3,820
Nitric acid	0-178,547	178,525	-648	178,525	-656
Ammonium nitrate	113,398-226,796	226,796	117	226,796	156
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	30,240	0
MAP	0-321,920	321,912		315,620	
DAP	0-2,062,100	2,062,100	2,137	2,021,801	2,095
GTSP	0-822,300	822,284	1,036	806,214	1,016
Contact process sulfuric acid	1,851,186-3,702,372	3,702,297	-14,963	3,698,313	-14,946
Wet process phosphoric acid	697,489-1,394,978	1,394,950	7,404	1,367,689	7,259
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
Ammonium sulfate	0-2,839,000	na	na	77,139	44
Acetic acid (standard)	0-8,165	8,165	111	0	0
Acetic acid (new)	0-8,165	na	na	8,165	92
Trona process for KCl	0-5,600,000	na	na	313,453	4,582
IMCC process for KCl	0-5,600,000	na	na	0	0
Sylvinitic process for KCl	0-5,600,000	47,159	895	0	0
Solid mixture	5,000 lower bound	163,859	0	1,098,536	0
Liquid mixture	5,000 lower bound	5,000	0	5,000	0
SO <sub>2</sub> recovery from gypsum	0-1,804,417	na	na	0	0
S & SO <sub>2</sub> recovery from gypsum	0-903,053	na	na	0	0
Ammonia sale		10,227		0	
Ammonium Nitrate sale		218,441		0	
Urea sale		0		0	
UAN sale		60,480		29,327	
MAP sale		321,912		315,620	
DAP sale		1,997,003		1,590,961	
GTSP sale		822,284		806,214	
Wet process phosphoric acid sale		13,950		13,677	
Methanol sale		177,080		181,437	
Total energy requirement			2,202		5,755

Production rates for the products in the optimal solution were constrained by their capacity limit, which were set at the Base Case 2 values. It was optimal to operate the ammonium sulfate. The energy requirement of ammonium nitrate plant in the optimal structure was different from base case with the same production rate. There are two reasons: one is the different production rate of two types of ammonium nitrate which are ammonium nitrate solution and granular ammonium nitrate; the other is the different temperatures of nitric acid from nitric acid plant to ammonium nitrate plant which also cause the different energy requirement for nitric acid plant.

The profit which includes the economic, environmental and sustainable costs increased about 8.57% from Base Case 2 to the optimal solution. Also, environmental cost increased about 5.26%, and sustainable costs increased about 2.08%. Energy requirements increased from 2202 to 5755 TJ/yr. The standard acetic acid plant consuming more energy in Base Case 2 was replaced by the new acetic acid plant in the optimal solution to reduce energy consumption. Similarly, the Sylvinitic plant (0.019 TJ/t) was replaced by the Trona plant (0.015TJ/t). The system selected plants for the complex with less energy requirements

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.

## Catalytic Process for Acetic Acid

**Capacity:** 100 million pound per year of acetic acid

36,700 tons per year of carbon dioxide raw material

### Savings

Reduction in utilities costs for process steam \$750,000

Energy savings from not having to produce this steam

275 trillion BTUs per year

Reduction in NOx emissions base on steam and power generation by cogeneration

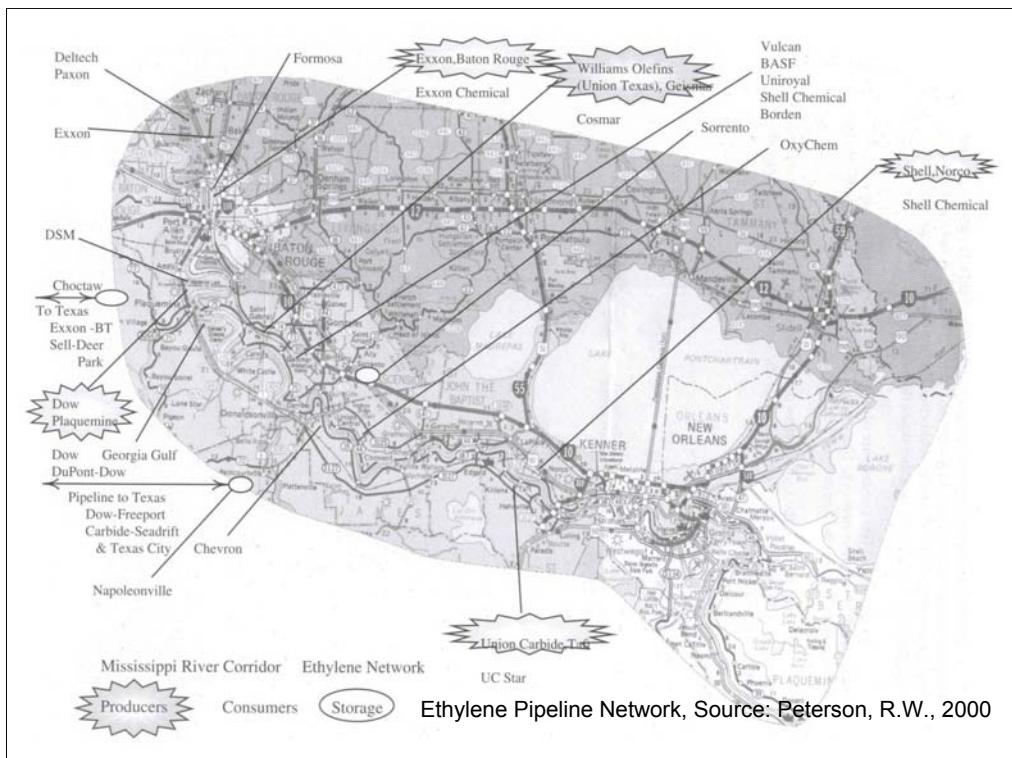
3.5 tons per year

Reduction in carbon dioxide emissions

12,600 tons per year from the steam production

36,700 tons per year conversion to a useful product

The new catalytic process for the direct conversion of carbon dioxide and methane to acetic acid was included in the optimal solution in place of the conventional process. This slide summarizes the savings from replacing the conventional process with the new one. There was a reduction in utility costs, energy savings from not having to produce steam for the acetic acid water separation and reductions in NOx and carbon dioxide emissions. Carbon dioxide emissions were reduced by the conversion of carbon dioxide to acetic acid and decreased steam production.



This map shows the ethylene pipeline network producers and consumers. Also, there are pipelines for ammonia, hydrogen and carbon dioxide. Diagram is from R. W. Peterson "Giants on the River" Homesite Company, Baton Rouge (1999).

## Carbon Dioxide Pipeline

Ammonia plants produce 0.8 million tons per year

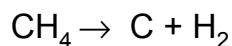
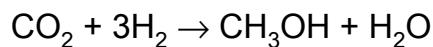
Methanol and urea plants consume 0.15 million tons per year

Surplus high purity carbon dioxide  
**0.65 million tons per year**  
**exhausted to atmosphere**

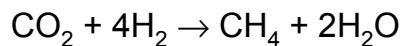
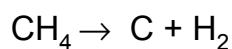
This slide shows that there is currently a surplus of high purity carbon dioxide from ammonia plants in the complex. It is exhausted to the atmosphere, now.

## Other Processes to Use Carbon Dioxide

Methanol from carbon dioxide and hydrogen with hydrogen from methane cracking



Graphite from carbon dioxide



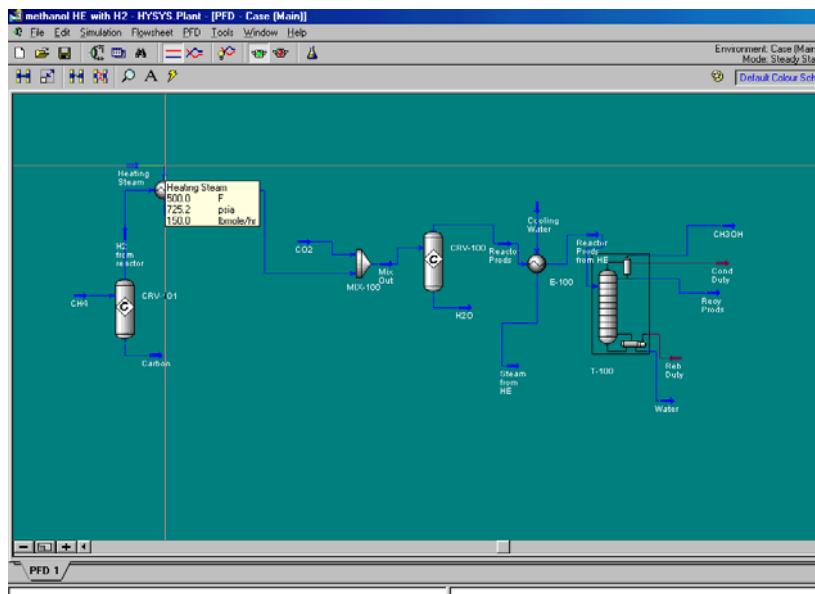
The catalytic process for acetic acid used 0.04 million tons per year of carbon dioxide process (36,700 tons per year), and additional processes are being evaluated to use this excess. We have completed evaluations on these two processes and will incorporate them in the complex.

## Develop Process Information for the System

- Simulate process using HYSYS.
- Estimate utilities required.
- Perform economic analysis.
- Obtain process constraint equations from HYSIS simulation.
- Maximize the profit function to find the optimum process configuration with the System.
- Incorporate into superstructure.

This slide shows the procedure to evaluate a potential process for incorporation into the system. A flowsheeting program, HYSIS, is used to develop the process flow diagram. The flowsheeting program determines the operating conditions and the utilities required, steam and cooling water. Then a value added economic analysis is performed to estimate the profitability of the plant. If the profitability is acceptable, then the process is entered in System using the material and energy balances, rate equations and equilibrium relations as equality constraints and demand for product, availability of raw material and capacities of the process units as inequality constraints. Results from the System give the optimum configuration of the process, and then this information is included in the superstructure of the complex.

HYSYS Simulation of Methanol Production Process



This slide shows a screen print of the HYSIS process flow diagram for the proposed methanol process.

## Constraints for Methanol Process

Process	Mass Yield	Demand for product (lb mole/h)	Availability of raw material (lbmole/h)
Reactor 1	0.175	$125 \leq \text{CH}_3\text{OH} \leq 175$	$300 \leq \text{CH}_4 \leq 400$
Reactor 2	1	$125 \leq \text{steam} \leq 175$	$150 \leq \text{CO}_2 \leq 200$

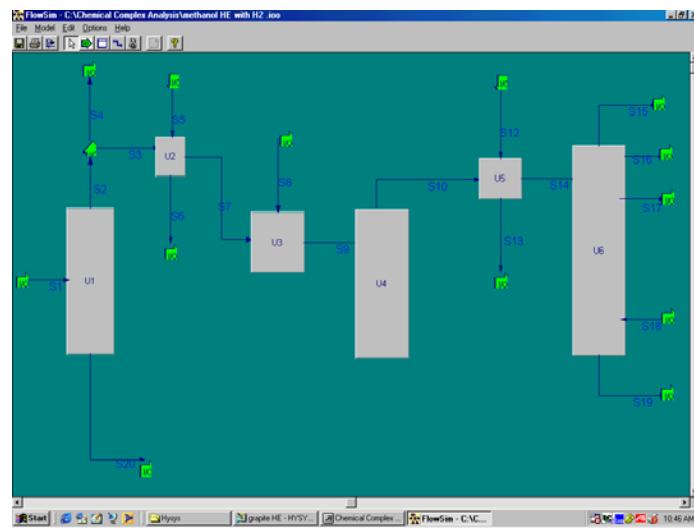
This slide shows the process constraints for the proposed plant.

## Economic Data for Methanol Process

Process	Feed	Cost (\$/kg)
Reactor 1	CH <sub>4</sub>	0.04
	Credit for CO <sub>2</sub> reuse	0.0065
	By product H <sub>2</sub>	5.34
Distillation Column	Product CH <sub>3</sub> OH	0.16
	By product steam	0.00865

This slide shows the economic data for the proposed methanol process. The proposed plant incorporates a H<sub>2</sub> production step for use in the reaction with carbon dioxide to produce methanol. Excess by-product hydrogen can be used as a feed stock in another process.

## Chemical Complex Analysis Flowsheet for Methanol Process



This slide shows the System process flow diagram for the proposed plant. The optimum profit and structure is obtained , and this information is evaluated to determine if the plant should be included in the superstructure of the complex.

## Optimum Process Conditions for Methanol Process

Name	Optimum	Stream_N	Process_U	Units_of_P	Description	
F1	6400	S1			CH4 FLOW RATE (lb/hr)	
F10	8163	S10			REACTOR PRODUCTS	
F14	8163	S14			REACTOR PRODS FROM HE	
F15	4000	S15			PRODUCT CH3OHFLOW RATE	
F19	3150	S19			BY PRODUCT STEAM	
F2	1120	S2			H2 FROM REACTOR	
F20	5280	S20			CARBON AND METHANE	
F3	977	S3			H2 TO HEAT EXCHANGER	
F4	142.7	S4			BY PRODUCT H2	
F7	977	S7			H2 TO MIXER	
F8	7186	S8			CO2 FEED RATE	
F9	8163	S9			MIX OUT	
profit (\$/hr)	557					

This slide shows the results from the System, and a reasonable profit is obtained. We are proceeding to incorporate this process in the superstructure.

## Conclusions

- The System has been applied to an extended agricultural chemical complex in the lower Mississippi River corridor
- Economic model incorporated economic, environmental and sustainable costs.
- An optimum configuration of plants was determined with increased profit and reduced energy and emissions
- For acetic acid production, new catalytic process is better than conventional process based on energy savings and the reduction of  $\text{NO}_x$  and  $\text{CO}_2$  emissions.

In conclusion, a System has been developed that determines the optimum configuration of plants from a superstructure and best energy use in the complex. It incorporates the AIChE Total Cost Assessment (TCA) for economic, energy, environmental and sustainable costs and incorporates EPA Pollution Index methodology (WAR) algorithm. The System has been used with an agricultural chemical complex in the lower Mississippi River corridor, and its capability has been demonstrated by determining the optimal configuration of units based on economic, environmental and sustainable costs.

The profit which includes the economic, environmental and sustainable costs increased about 8.58% from Base Case 1 to the optimal solution, also environmental cost increased about 5.24%, and sustainable costs increased about 2.18%. Also the energy requirements increased from 2092 to 5663 TJ/yr. The sylvinitic plant (0.019 TJ/t) consuming more energy in Base Case 1 was replaced by the Trona plant (0.015 TJ/t) in the optimal solution to reduce energy consumption.

The profit which includes the economic, environmental and sustainable costs increased about 8.57% from Base Case 2 to the optimal solution. Also, environmental cost increased about 5.26%, and sustainable costs increased about 2.08%. Energy requirements increased from 2202 to 5755 TJ/yr. The standard acetic acid plant consuming more energy in Base Case 2 was replaced by the new acetic acid plant in the optimal solution to reduce energy consumption. Similarly, the Sylvinitic plant (0.019 TJ/t) was replaced by the Trona plant (0.015 TJ/t). The system selected plants for the complex with less energy requirements

## Conclusions

- 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 manuals and tutorials. These can be downloaded at no cost from the LSU Mineral Processing Research Institute's web site [www.mpri.lsu.edu](http://www.mpri.lsu.edu)

The System could be applied to other chemical complexes, and the System is available at no charge from the LSU Minerals Processing Research Institute, [www.mpri.lsu.edu](http://www.mpri.lsu.edu).

## Future Work

- Add new processes for carbon dioxide
- Expand to a petrochemical complex in the lower Mississippi River corridor
- Add processes that produce fullerines and carbon nanotubes

This work is continuing by adding new plants that use greenhouse gases as raw materials. The complex is being expanded to have a petrochemical complex by adding other plants in the region. Also, processes for fullerines and carbon nanotubes are being evaluated for inclusion in the complex. These potential processes are high temperature and energy intensive. They will need the infrastructure, raw materials and energy available in these chemical complexes.