

NATO CCMS Pilot Study on Clean Products and Processes  
2003 Annual Meeting, May 11 - 15, 2003  
Hotel San Michele, Cetraro, Italy

## Development and Integration of New Processes for Greenhouse Gases Management in Multi-Plant, Chemical Production Complexes

T. A. Hertwig<sup>a</sup>, A. Xu<sup>b</sup>, D. B. Ozyurt<sup>b</sup>, S. Indala<sup>b</sup>, R. W. Pike<sup>b</sup>, F. C. Knopf<sup>b</sup>, J. R. Hopper<sup>c</sup>,  
and C. L. Yaws<sup>c</sup>

a IMC Phospates, Uncle Sam, LA 70792, tahertwig@imcglobal.com

b Louisiana State University, Louisiana State University, pike@che.lsu.edu, axu1@lsu.edu, knopf@che.lsu.edu

c Lamar University, Beaumont, TX 77710, hopperjr@hal.lamar.edu, yawscl@hal.lamar.edu

### 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 on the AIChE Total Cost Assessment (TCA) for economic, energy, environmental and sustainable costs and incorporates EPA Pollution Assessment 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.

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 to acetic acid 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, 3.5 tons per year in NO<sub>x</sub> and 49,100 tons per year in carbon dioxide emissions.

This System was developed in collaboration with process engineers and 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 Advanced Process Analysis System is used to perform economic and environmental evaluations of a plant. The main components of this system are a flowsheeting program, an on-line optimization program, a chemical reactor analysis program, a heat exchanger network design program, and a pollution assessment module. A Windows interface has been used to integrate these programs into one user-friendly application. An accurate description of the process is obtained from process flowsheeting and on-line optimization. Then an evaluation of the best types of chemical reactors is performed to modify and improve the process, and pinch analysis is used to determine the best configuration for the heat exchanger network and determine the minimum utilities needed for the process. The pollution index evaluation is used to identify and minimize emissions. A tutorial has two plant simulations and two actual plants.

The Advanced Process Analysis System has been applied to actual plants including the alkylation plant at the Motiva refinery in Convent, Louisiana and sulfuric acid contact plant at IMC Agrico's agricultural chemicals complex in Uncle Sam, Louisiana. Detailed plant descriptions of the refinery alkylation process and the contact sulfuric acid process were used with the System in collaboration with the process engineers from these companies. This ensured that the programs work on actual plants and meet the needs and requirements of the process and design engineers.

These programs and users manuals with tutorials can be obtained from the LSU Minerals Processing Research Institute's web site, [www.mpri.lsu.edu](http://www.mpri.lsu.edu) at no charge. The staff of the Minerals Processing Research Institute can provide assistance in using these programs.

# Development and Integration of New Processes for Greenhouse Gases Management in Multi- Plant, Chemical Production Complexes

T. A. Hertwig, A. Xu, D. B. Ozyurt, S. Indala R.W. Pike,  
F. C. Knopf, J. R Hopper, and C. L. Yaws

A joint industry-university research effort  
IMC Phosphates, Motiva Enterprises,  
Louisiana State University, Lamar University

Sponsored by U. S. Environmental Protection Agency

NATO CCMS Pilot Study on Clean Products and Processes

2003 Annual Meeting, May 11 - 15, 2003

Hotel San Michele, Cetraro, Italy

# LSU Mineral Processing Research Institute

Minerals Processing Research Institute


Minerals Processing Research Institute

setpoints for controllers

Distributed Control System

optimal operating conditions

setpoint targets





Louisiana State University

**Mission** Processing, economic and environmental research for the main mineral of the State: oil and natural gas, and for sulfur, salt and lignite.

**History** Formed in 1979 as one of 31 U.S. Department of Interior State Mineral Institutes.

**Research Directions** Focus on minerals processing research for chemical plants and petroleum refineries. Cooperative agreements are in place with IMC Agrico, Monsanto, and Motiva (formerly Star/Texaco).

Home  
Research Emphasis  
Collaboration  
Computer Programs  
Research Results  
Internet Courses  
Text Book  
Industry Associates  
Staff  
Contact



All of the information given in this presentation is available at  
[www.mpri.lsu.edu](http://www.mpri.lsu.edu)

# Background

## 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 (economic and ecological)

# Broader Assessment of Current and Future Manufacturing in the Chemical Industry

## Driving forces

ISO 14000,

“the polluter pays principle”

Anticipated next round of Federal regulations associated with global warming

Sustainable development

## Sustainable development

Concept that development should meet the needs of the present without sacrificing the ability of the future to meet its needs

## Sustainable development costs - external costs

Costs that are not paid directly

Those borne by society

Includes deterioration of the environment by pollution within compliance regulations.

Koyoto Protocol - annual limits on greenhouse gases proposed beginning in 2008 - 7% below 1990 levels for U.S.

# Overview of Presentation

Chemical Complex and Cogeneration Analysis System  
for multi-plant chemical production complexes

Advanced Process Analysis System  
for operating plants

# 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



# 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](http://www.oit.doe.gov/bestpractice)
- Environmental Protection Agency (EPA)  
[www.epa.gov/opptintr/greenengineering](http://www.epa.gov/opptintr/greenengineering)

# Chemical Complex and Cogeneration Analysis System

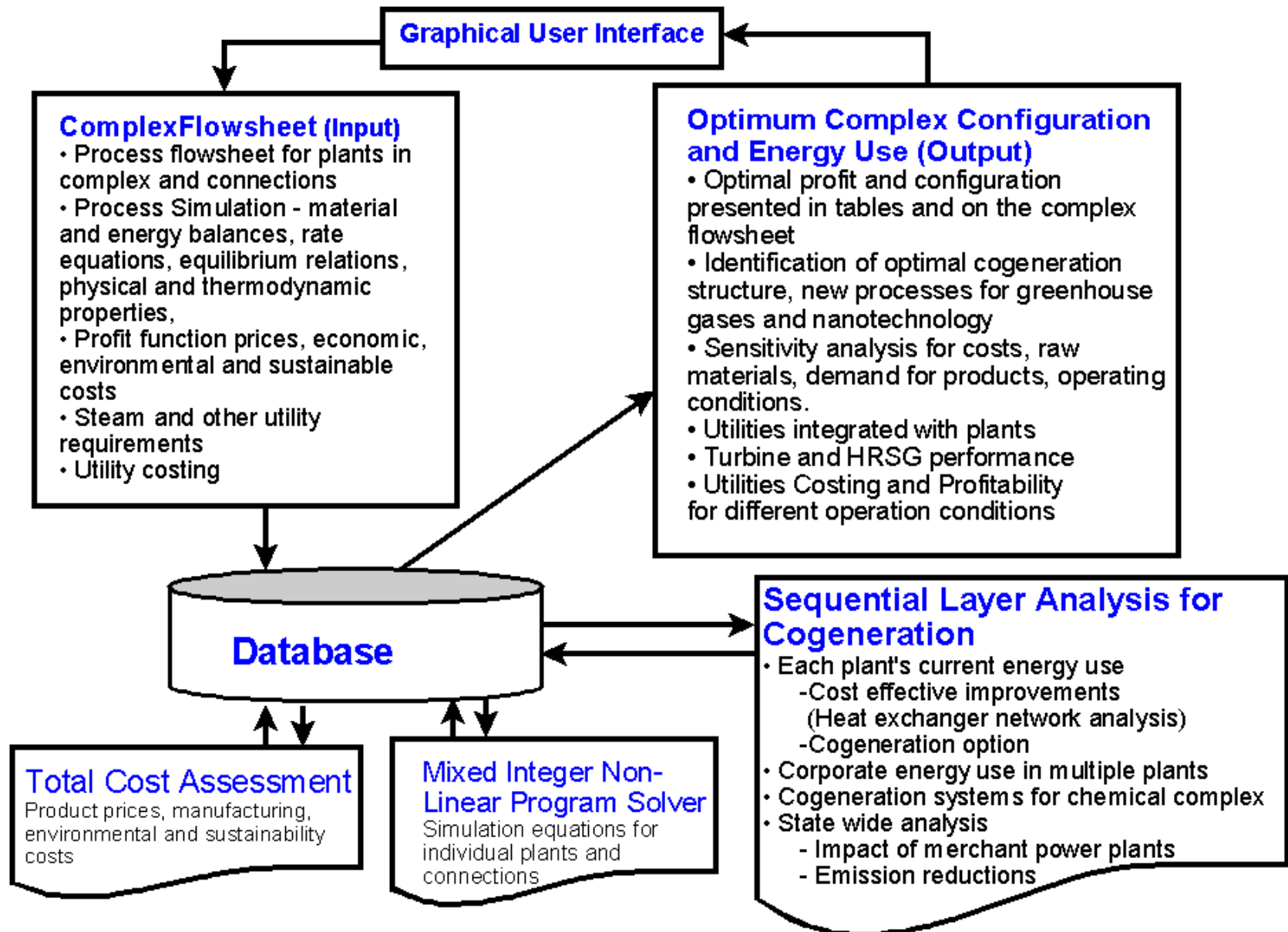
## **Chemical Complex Analysis System**

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.

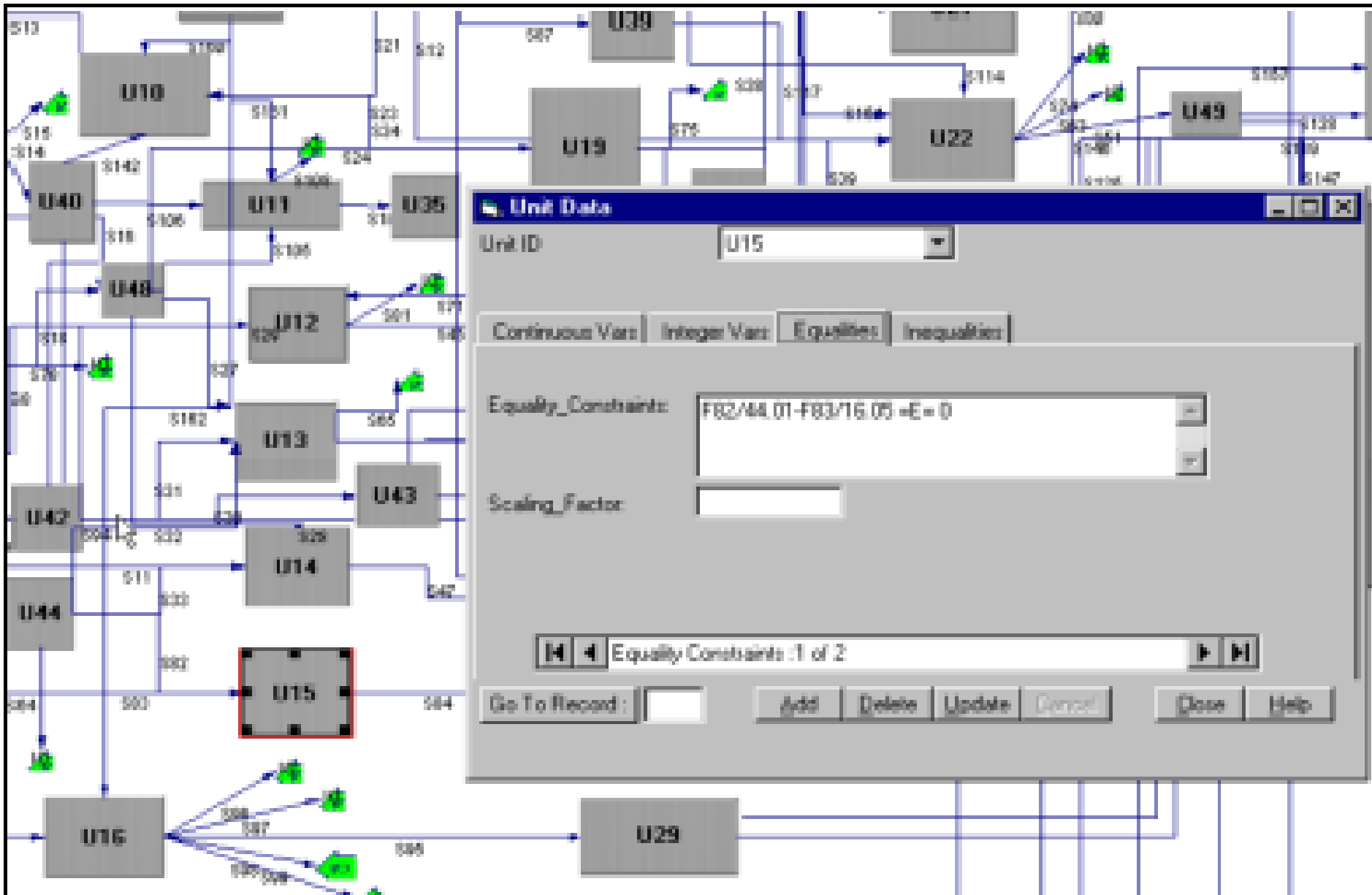
# Structure of the System



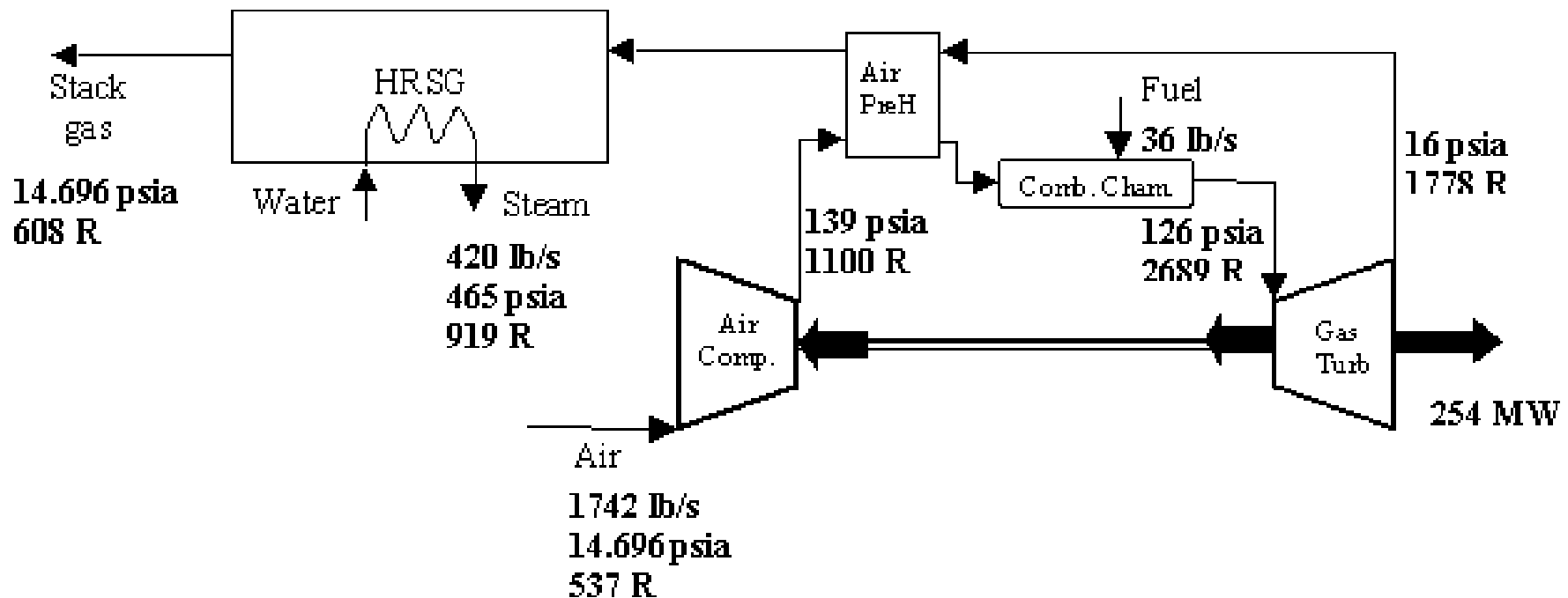
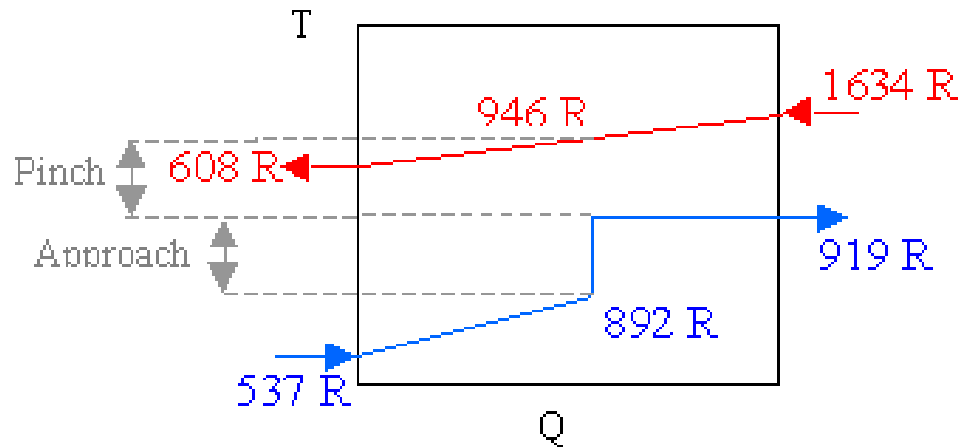
# AIChE Total Cost Assessment

- 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

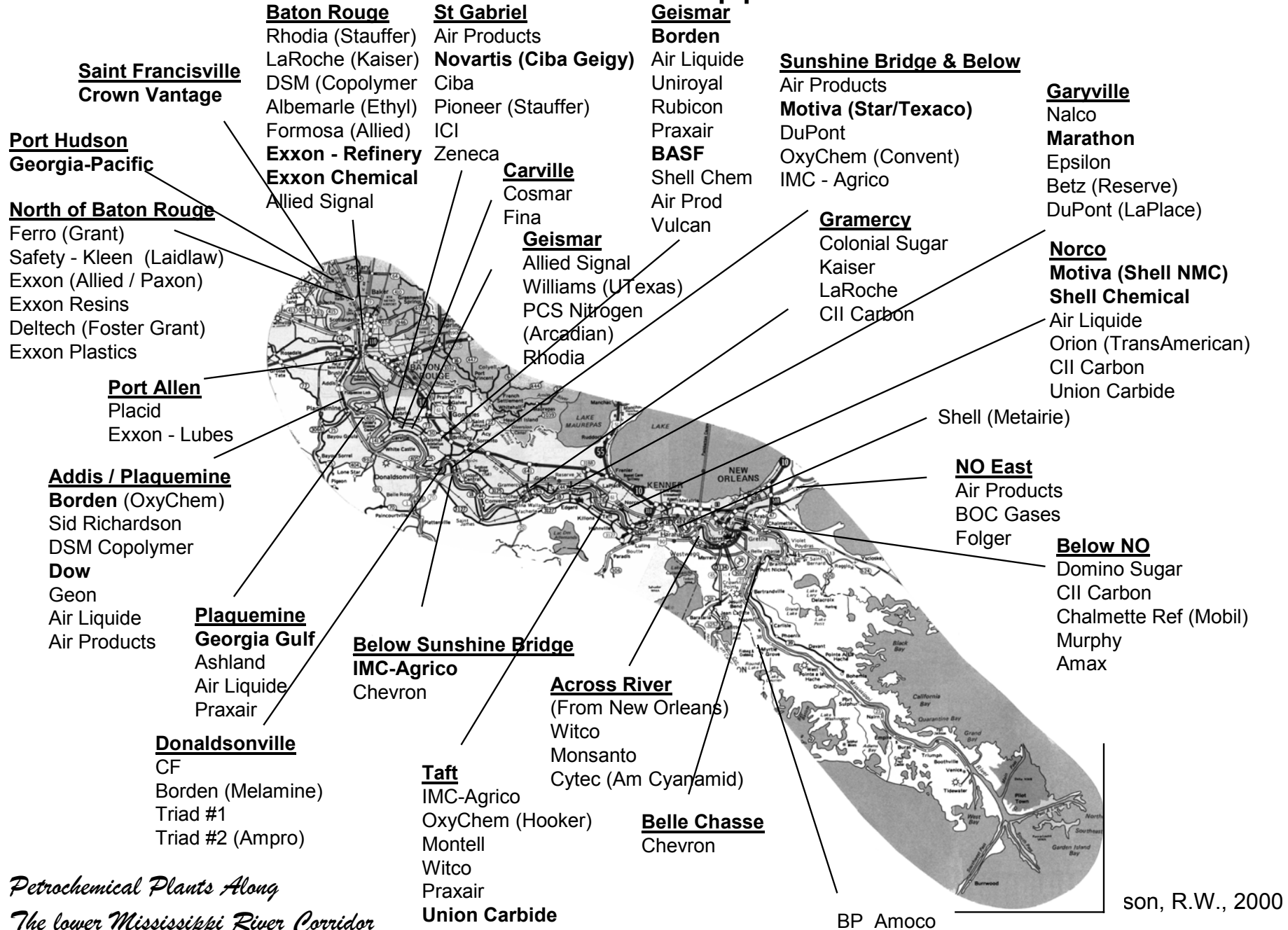


# Comparison of Power Generation

	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

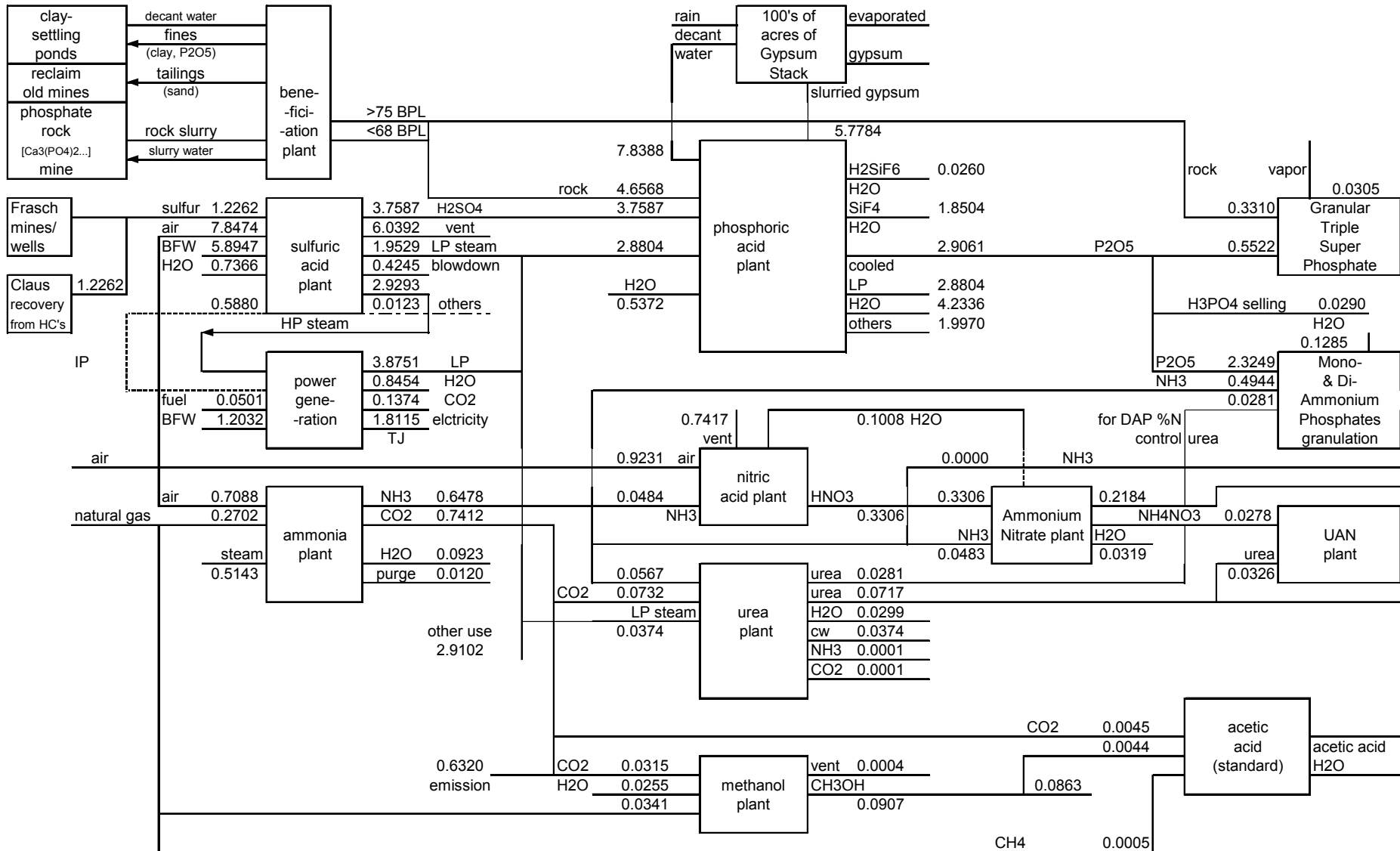


# Plants in the lower Mississippi River Corridor



*Petrochemical Plants Along  
The lower Mississippi River Corridor*

# Expanded Agricultural Chemical Complex

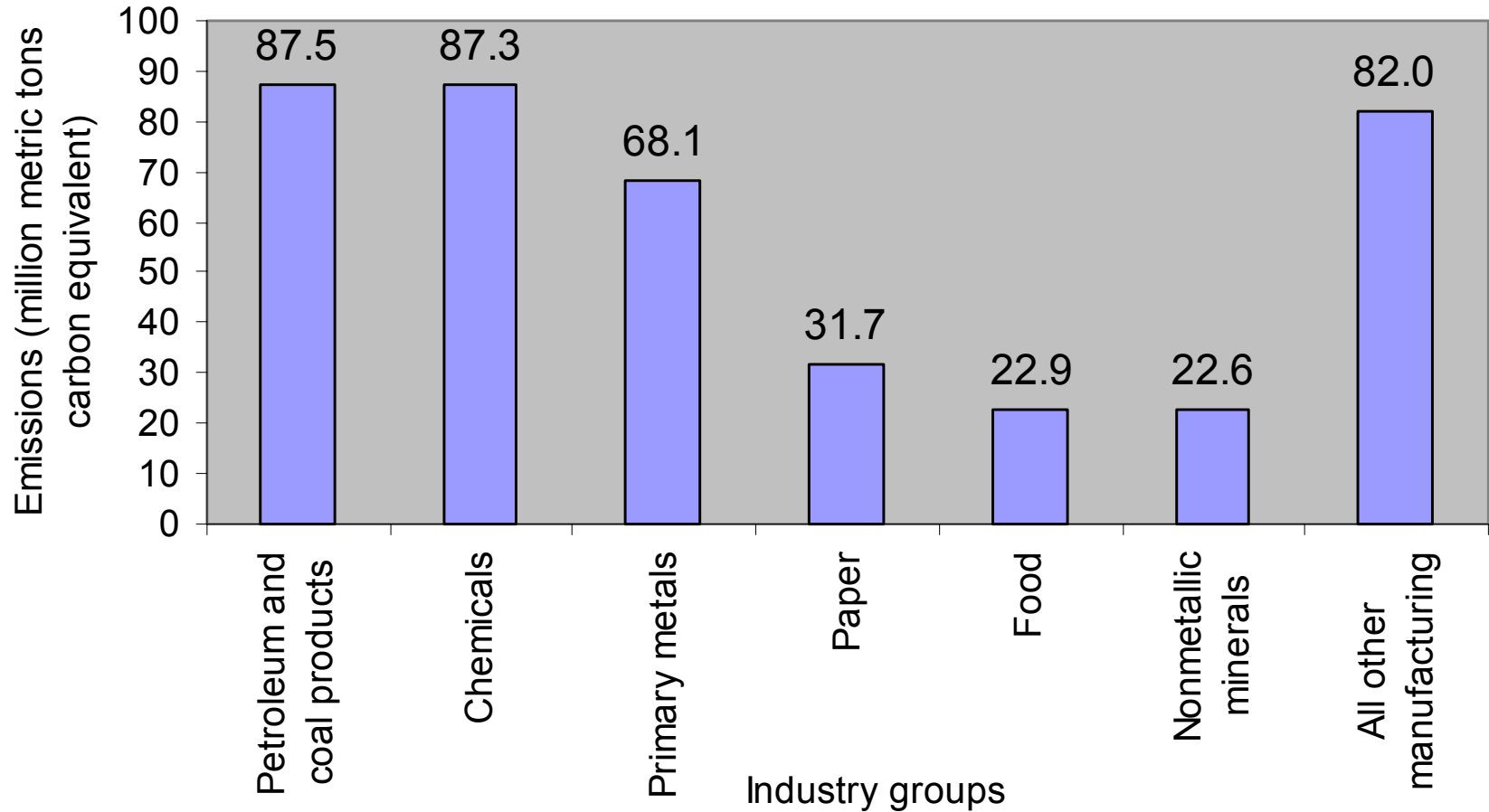


Plants in the lower Mississippi River Corridor, Base Case. Flow Rates in Million Tons Per Year

# Some 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

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



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

# 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 Burning fossil fuels                      5,500 Deforestation	IPCC (1995)
Total worldwide CO <sub>2</sub> from consumption and flaring of fossil fuels United States                      1,600 China Russia Japan All others	EIA (2002)
U.S. CO <sub>2</sub> emissions Industry                      792 Buildings                      440 Transportation                      307 Total                      1,526	Stringer (2001)
U.S. industry (manufacturing ) Petroleum, coal products, and chemicals	EIA (2001)
Chemical and refinery (BP) Combustion and flaring                      1,627 Noncombustion direct CO <sub>2</sub> emission                      3%	McMahon (1999)
Agricultural chemical complex in the lower Mississippi River corridor excess high purity CO <sub>2</sub> 97%	Hertwig et al. (2002)
CO <sub>2</sub> used in chemical synthesis	Arakawa et al. (2001)

# 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

# Surplus Carbon Dioxide

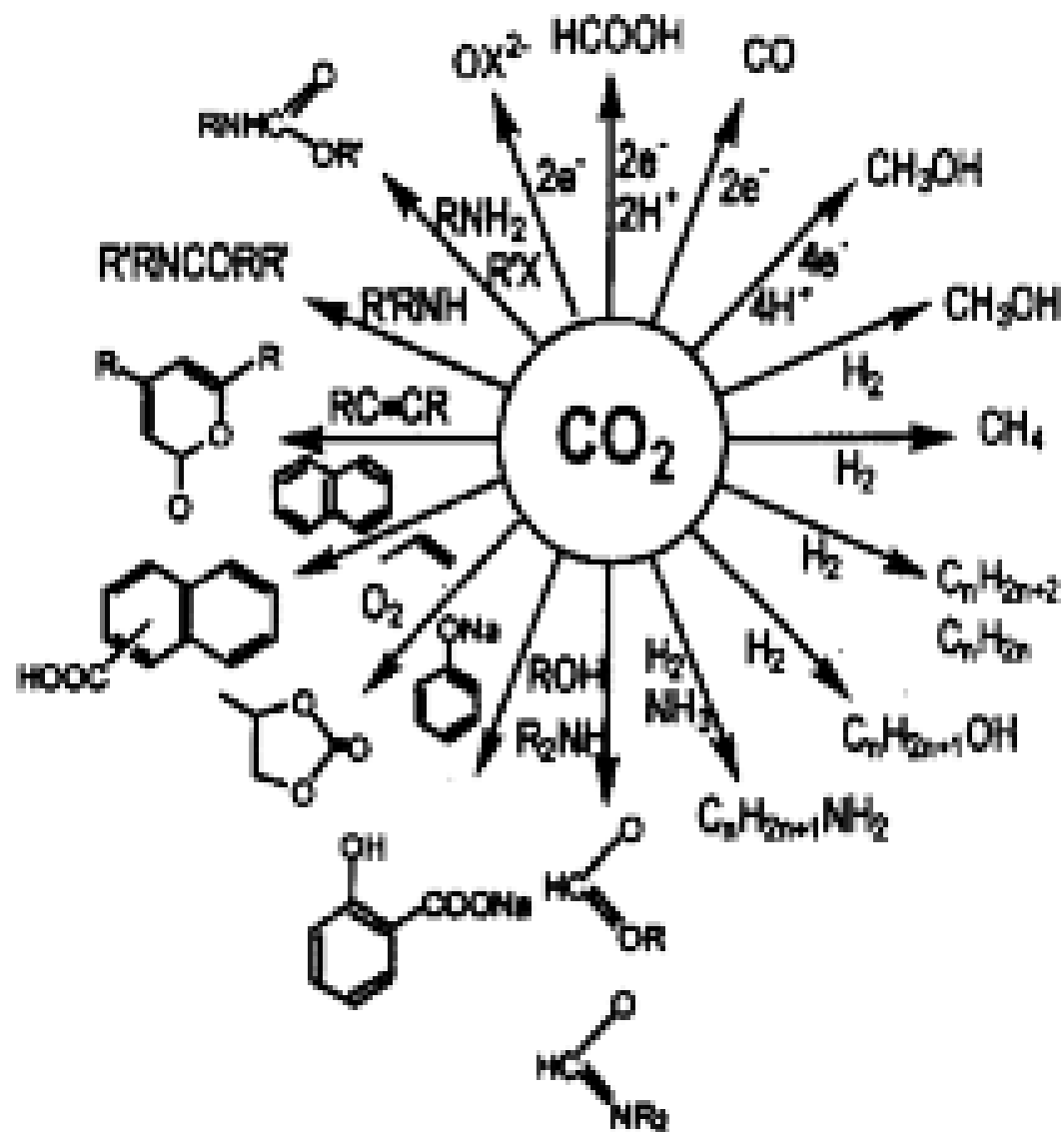
Ammonia plants produce 1.2 million tons per year in lower Mississippi River corridor

Methanol and urea plants consume 0.15 million tons per year

Surplus high-purity carbon dioxide 1.0 million tons per year vented to atmosphere

# 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<sub>3</sub>OH

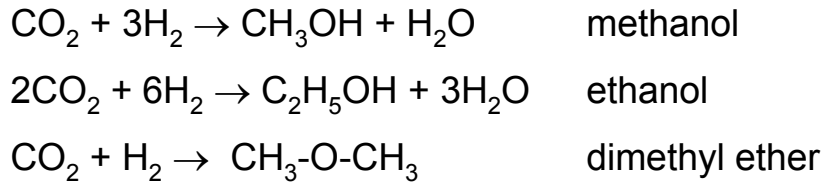


From Creutz and Fujita, 2000

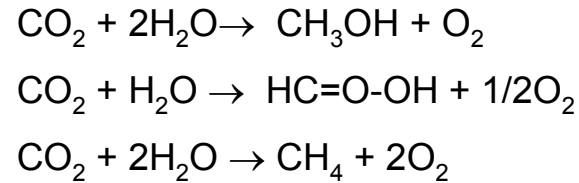


# Catalytic Reactions of CO<sub>2</sub> from Various Sources

## Hydrogenation



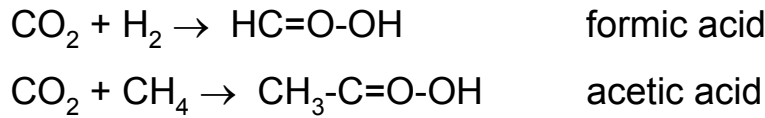
## Hydrolysis and Photocatalytic Reduction



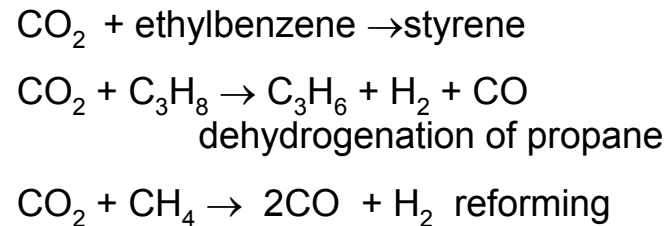
## Hydrocarbon Synthesis



## Carboxylic Acid Synthesis



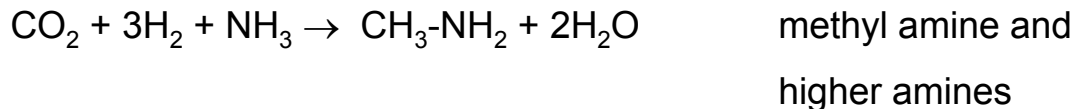
## Other Reactions



## Graphite Synthesis



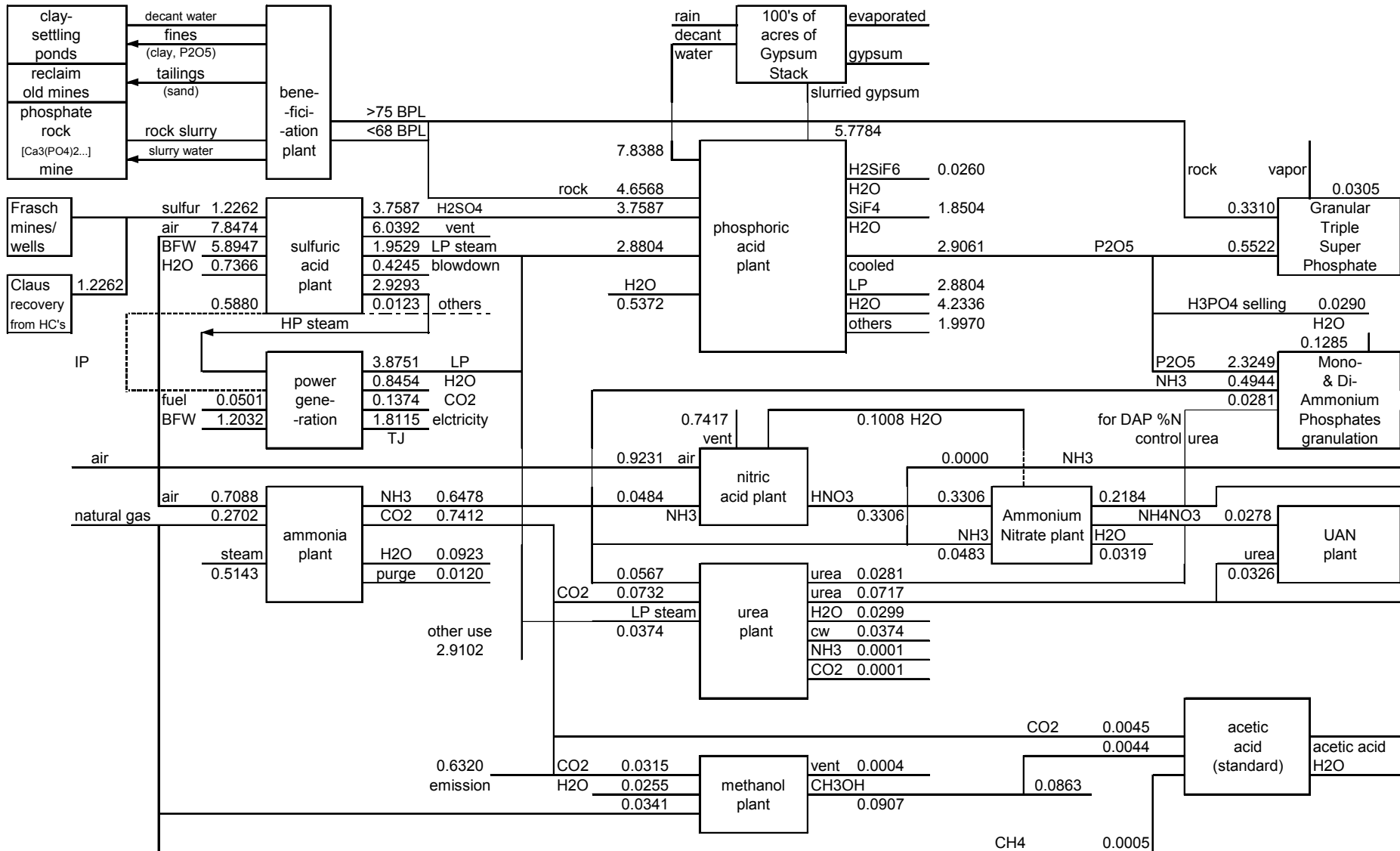
## Amine Synthesis



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

- Base case
- Superstructure
- Optimal structure

# Base Case of Actual Plants

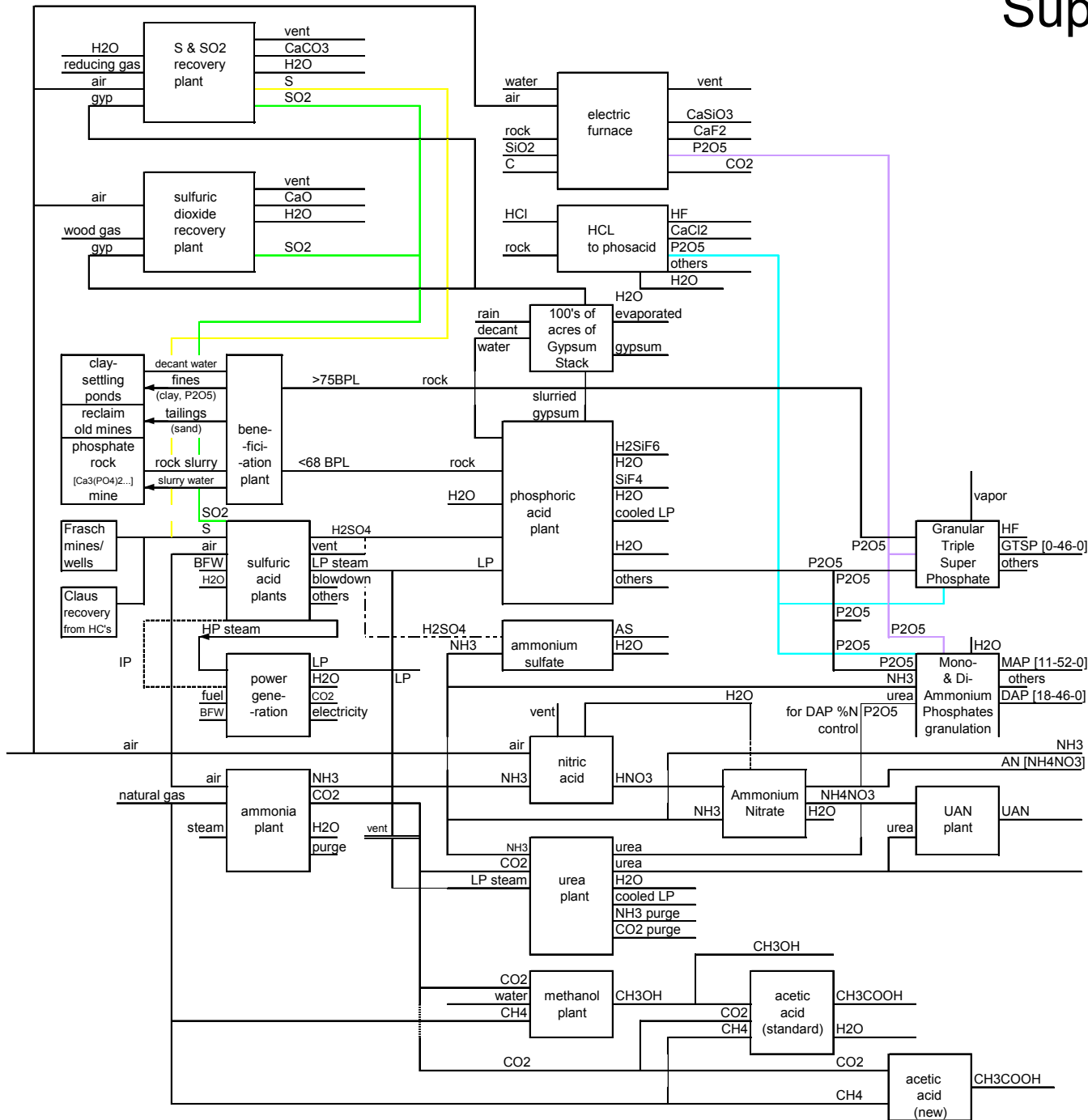


Plants in the lower Mississippi River Corridor, Base Case. Flow Rates in Million Tons Per Year

# Processes in the Superstructure

Processes in Superstructure	
Processes in Base Case	Electric furnace process for phosphoric acid
Ammonia	HCl process for phosphoric acid
Nitric acid	Ammonium sulfate
Ammonium nitrate	SO <sub>2</sub> recovery from gypsum process
Urea	S & SO <sub>2</sub> recovery from gypsum process
UAN	Acetic acid – new CO <sub>2</sub> -CH <sub>4</sub> catalytic process
Methanol	
Granular triple super phosphate	
MAP & DAP	
Power generation	
Contact process for Sulfuric acid	
Wet process for phosphoric acid	
Acetic acid-conventional process	

# Superstructure



# Superstructure Characteristics

## Options

- Three options for producing phosphoric acid
- Two options for producing acetic acid
- 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

594 continuous variables

7 integer variables

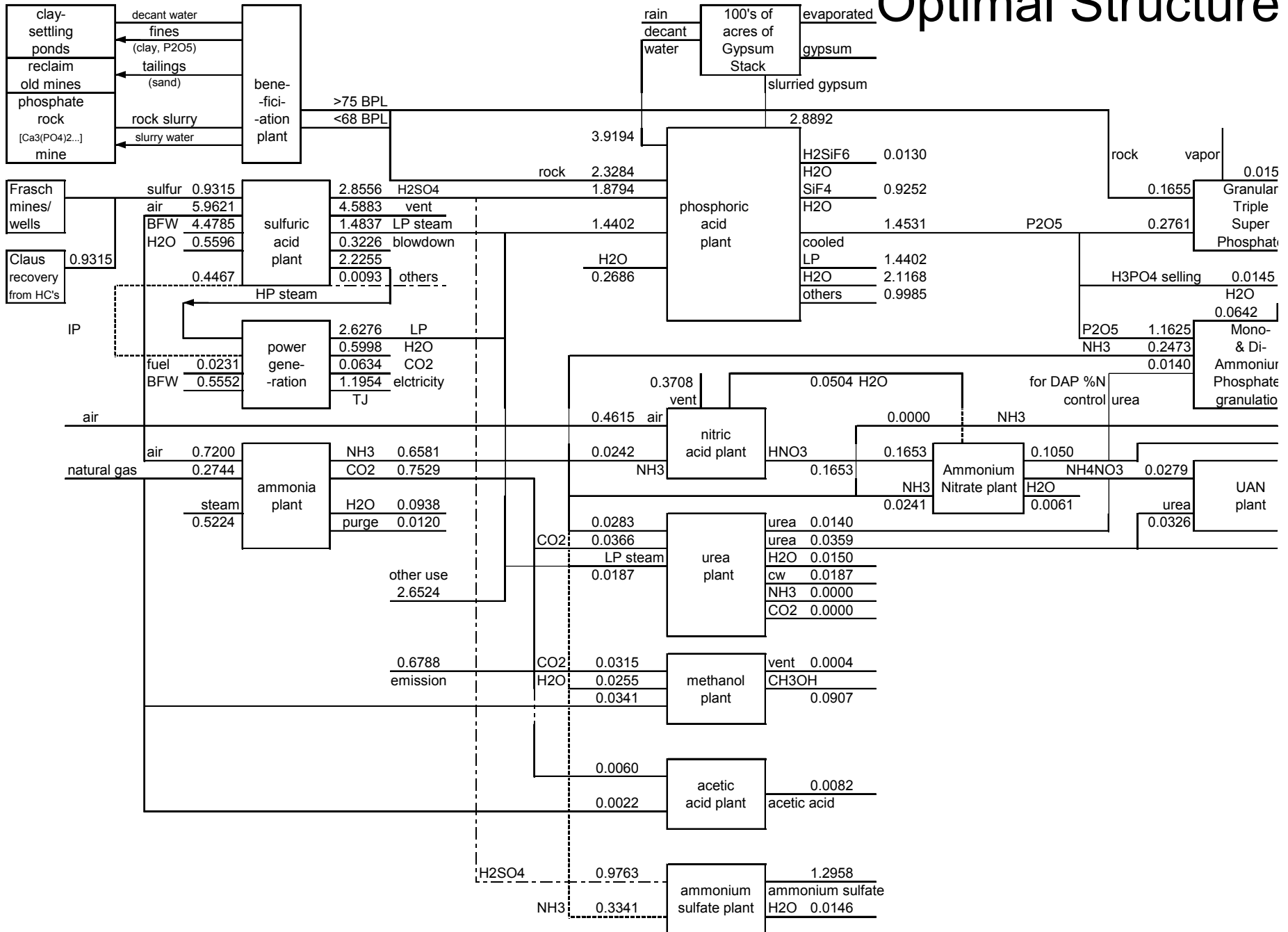
505 equality constraint equations  
for material and energy balances

27 inequality constraints for availability of raw materials  
demand for product, capacities of the plants in the complex

# Raw Material and Product Prices

<u>Raw Materials</u>	<u>Cost (\$/mt)</u>	<u>Raw Materials</u>	<u>Cost (\$/mt)</u>	<u>Products</u>	<u>Price (\$/mt)</u>	
Natural Gas	245	Market cost for short term purchase		Ammonia	190	
Phosphate Rock		Reducing gas		Methanol	96	
wet process		Wood gas		Acetic Acid	623	
electrofurnace	24	<u>Sustainable Costs and Credits</u>			GTSP	
HCl process	25	Credit for CO <sub>2</sub> Consumption	1394	MAP	180	
GTSP process	27	Debit for CO <sub>2</sub> Production	6.50	DAP		
HCl		Credit for HP Steam		4NO <sub>3</sub>	142	
Sulfur		Credit for IP Steam	3.25	UAN		
Frasch				Urea	165	
Claus	38			H <sub>3</sub> PO <sub>4</sub>	153	
C electrofurnace	42		6.4	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	187	
50		Credit for gypsum Consumption	10		320	
		Debit for gypsum Production	5			
		Debit for NO <sub>x</sub> Production	2.5			
			1025			

# Optimal Structure





# Comparison of Base Case and Optimal Structure

		Base case		Optimal structure	
Profit (U.S.\$/year)		148,087,243		246,927,825	
Environmental cost (U.S.\$/year)		179,481,000		123,352,900	
Sustainability cost (U.S.\$/year)		-17,780,800	energy	-16,148,900	energy
Plant name	Capacity (mt/year) (upper-lower bounds)	Capacity (mt/year)	requirement (TJ/year)	Capacity (mt/year)	requirement (TJ/year)
Ammonia	329,030-658,061	647,834	3,774	658,061	3,834
Nitric acid	0-178,547	178,525	-649	89,262	-324
Ammonium nitrate	113,398-226,796	226,796	116	113,398	26
Urea	49,895-99,790	99,790	127	49,895	63
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	1,063
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	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	1,295,770	726
Acetic acid (standard)	0-8,165	8,165	268	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
Ammonia sale		0		0	
Ammonium Nitrate sale		218,441		105,043	
Urea sale		39,076		3,223	
Wet process phosphoric acid sale		13,950		6,975	
Methanol sale		86,361		90,719	
Total energy requirement from fuel gas			2,912		1,344

# 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

# 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

# Catalytic Process for Acetic Acid

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

36,700 tons per year of carbon dioxide raw material

## Potential 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 NO<sub>x</sub> emissions base on steam and power generation  
by cogeneration

3.5 tons per year

Reduction in carbon dioxide emissions

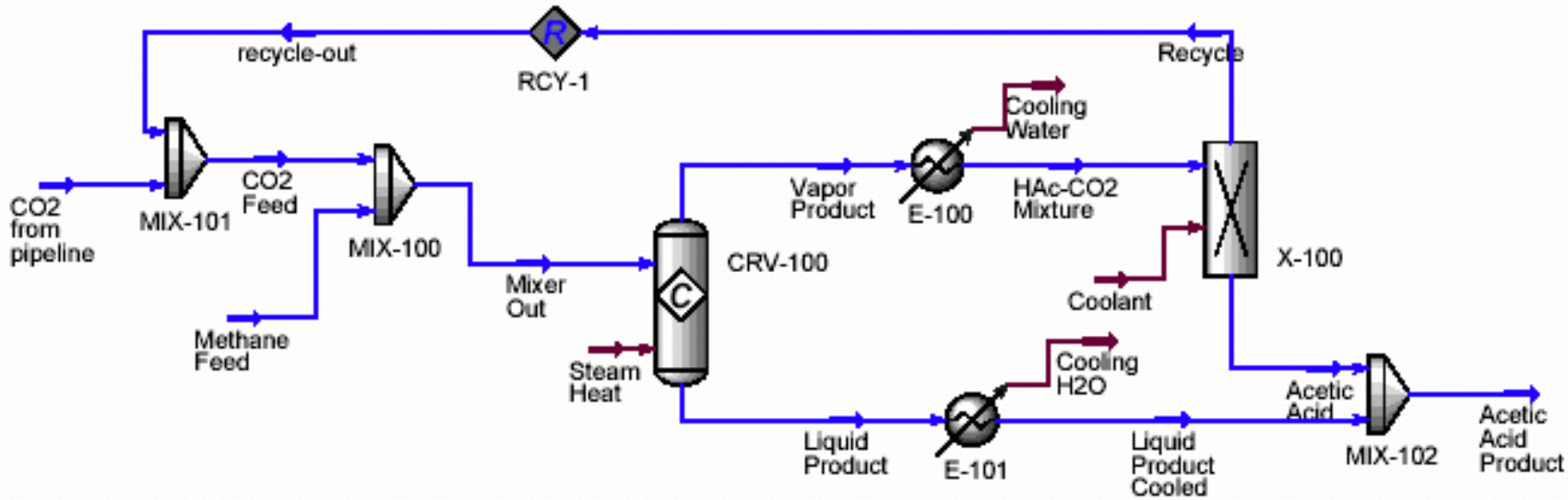
12,600 tons per year from the steam production

36,700 tons per year conversion to a useful product

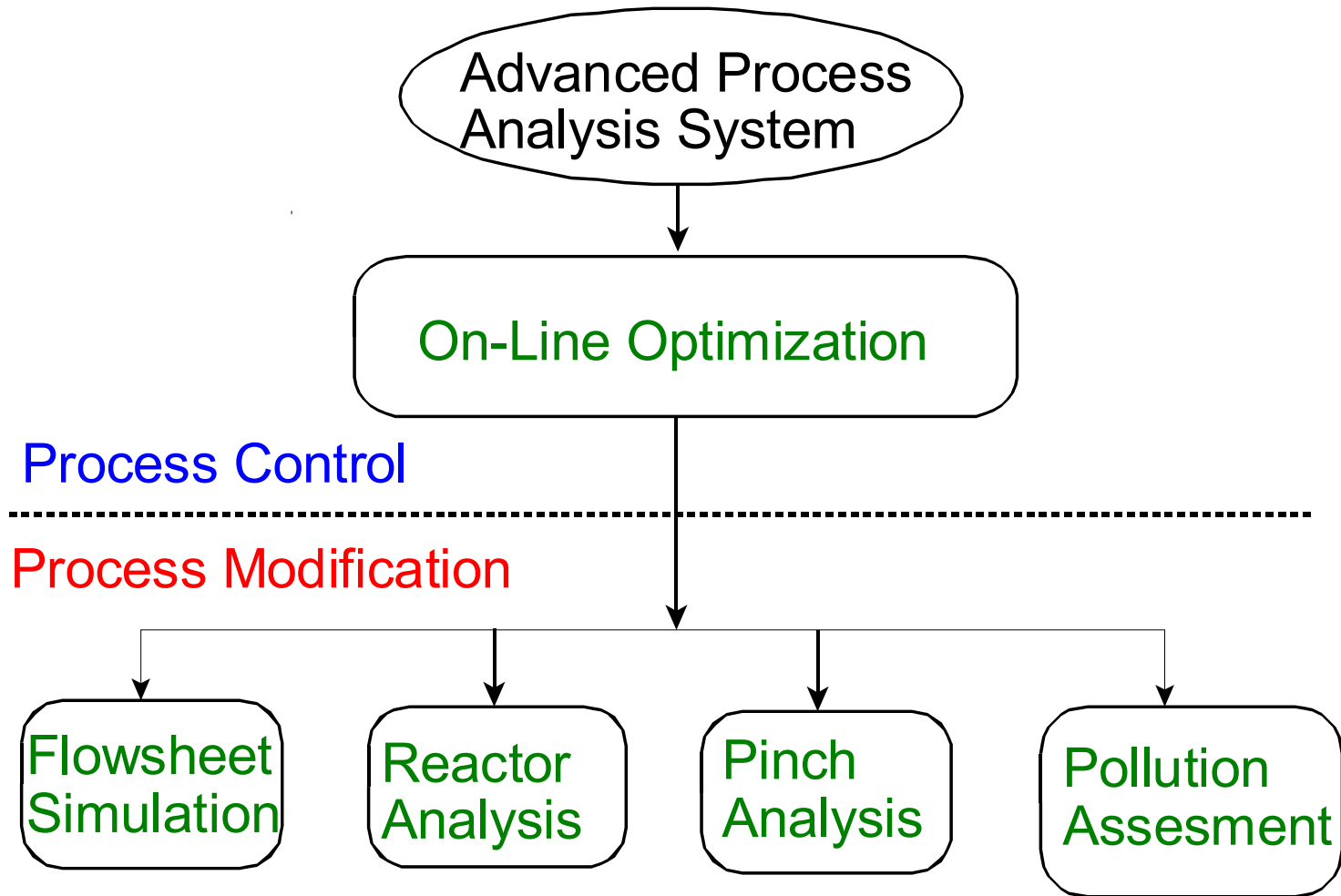
# Develop Process Information for the System

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

# HYSYS Process Flow Diagram for Acetic Acid Process

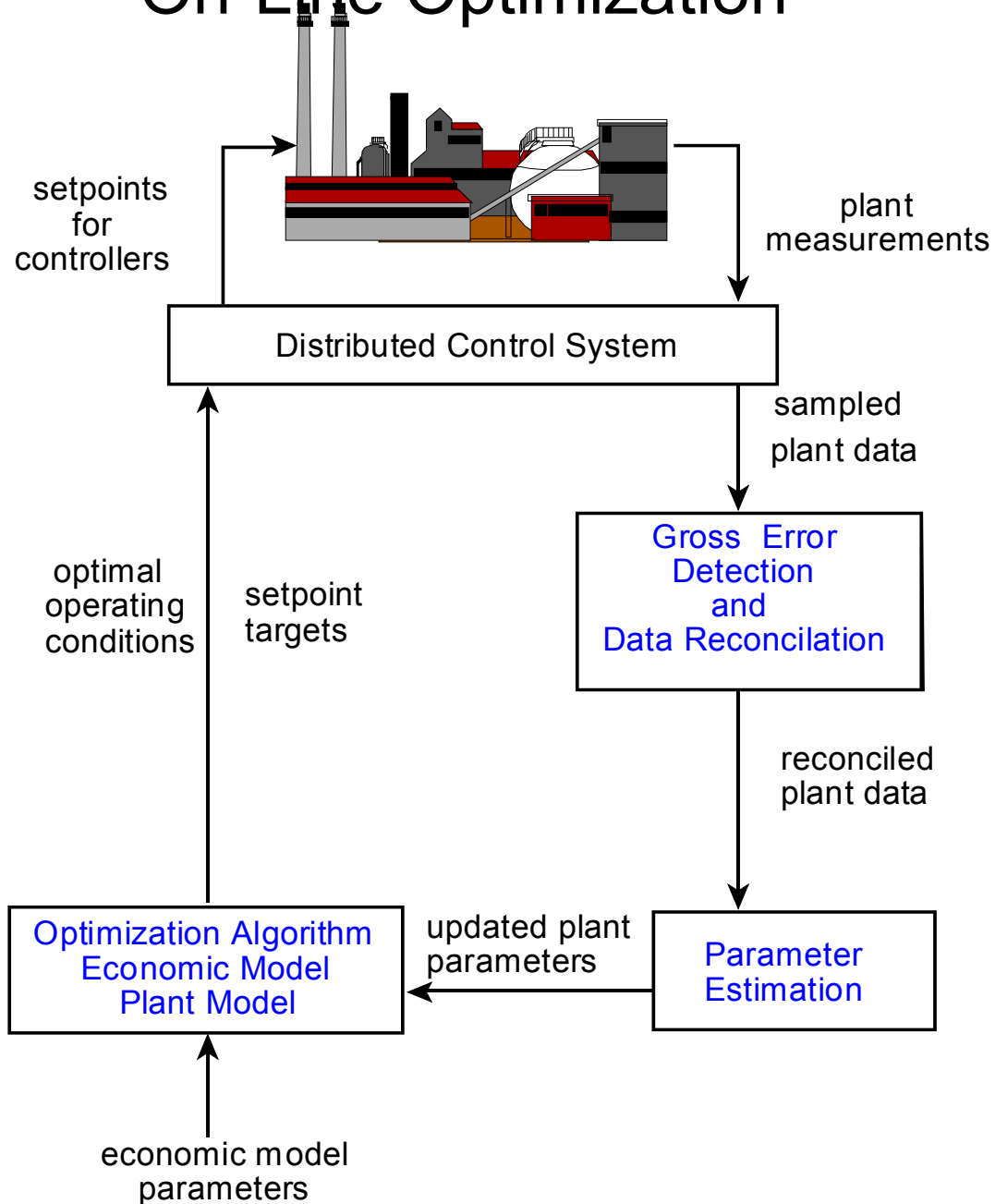


# Advanced Process Analysis System



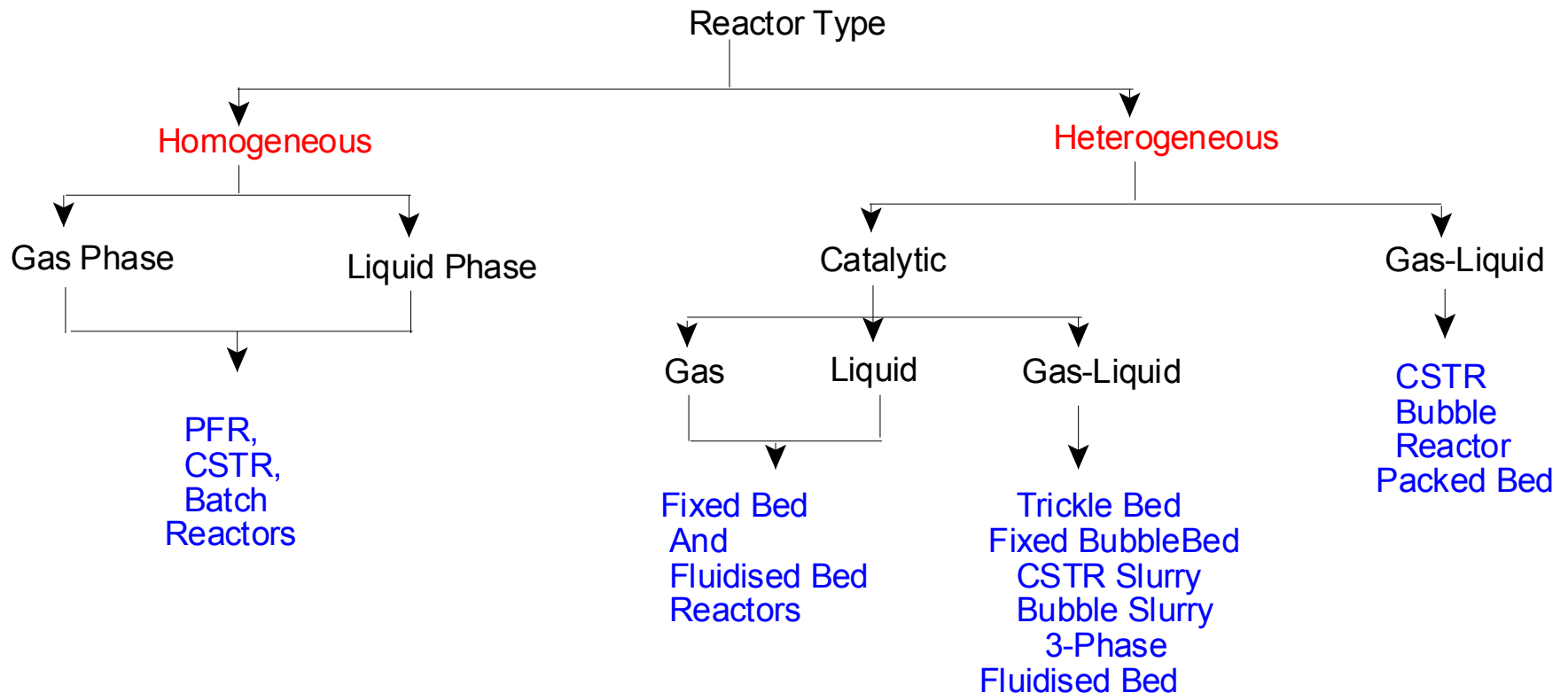
*Fig. 1 Overview of Advanced Process Analysis System*

# On-Line Optimization

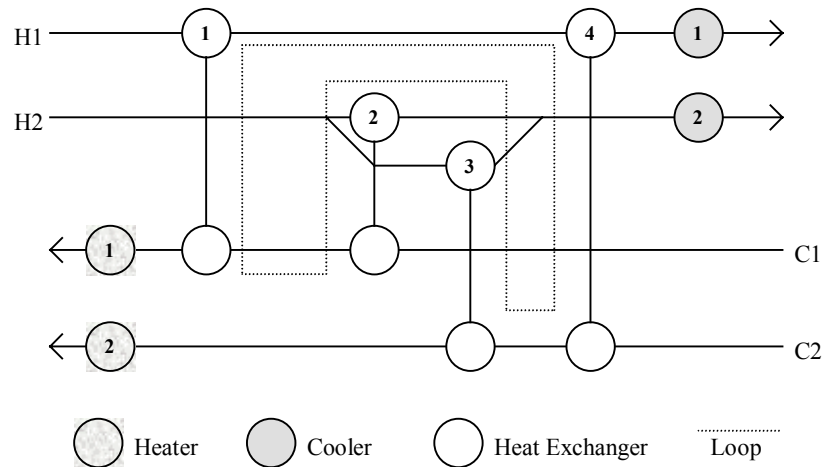
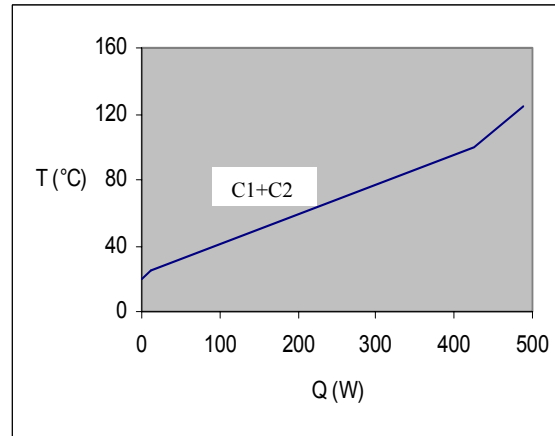
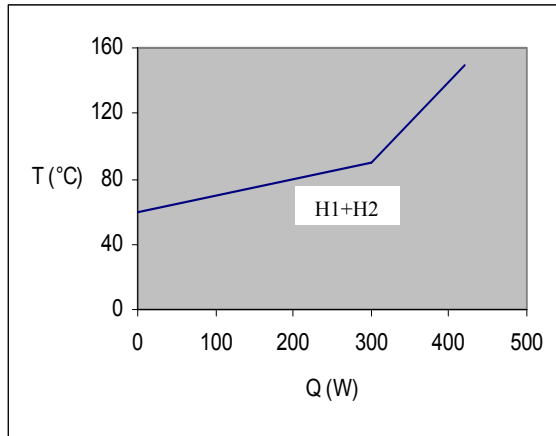




# Reactor Analysis



# Energy Integration – Pinch Analysis



# Pollution Assessment

## Waste Reduction Algorithm (WAR) and Environmental Impact Theory

### Pollution Index

$$I = \text{wastes/products} = - (\Sigma \text{Out} + \Sigma \text{Fugitive}) / \Sigma P_n$$

### Potential Environmental Impact

$$\Psi_k = \sum_l \alpha_l \Psi_{k,l}^s$$

$\alpha_l$  relative weighting factor

$\Psi_{k,l}^s$  units of potential environmental impact/mass of chemical k

# 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.

# 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)

# Future Work

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