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

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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 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 evaluates 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\textsubscript{x} 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 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


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
Hotel San Michele, Cetraro, Italy
LSU Mineral Processing Research Institute

All of the information given in this presentation is available at 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

• Environmental Protection Agency (EPA)
  www.epa.gov/opptintr/greenengineering
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

ComplexFlowsheet (Input)
- Process flowsheet for plants in complex and connections
- Process Simulation - material and energy balances, rate equations, equilibrium relations, physical and thermodynamic properties,
- Profit function prices, economic, environmental and sustainable costs
- Steam and other utility requirements
- Utility costing

Optimum Complex Configuration and Energy Use (Output)
- Optimal profit and configuration presented in tables and on the complex flowsheet
- Identification of optimal cogeneration structure, new processes for greenhouse gases and nanotechnology
- Sensitivity analysis for costs, raw materials, demand for products, operating conditions.
- Utilities integrated with plants
- Turbine and HRSG performance
- Utilities Costing and Profitability for different operation conditions

Database

Total Cost Assessment
Product prices, manufacturing, environmental and sustainability costs

Mixed Integer Non-Linear Program Solver
Simulation equations for individual plants and connections

Sequential Layer Analysis for Cogeneration
- Each plant's current energy use
  - Cost effective improvements
    (Heat exchanger network analysis)
  - Cogeneration option
- Corporate energy use in multiple plants
- Cogeneration systems for chemical complex
- State wide analysis
  - Impact of merchant power plants
  - Emission reductions

Graphical User Interface
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

Equality Constraints: F82/44.01 - F83/16.05 = E = 0

Scaling Factor:
Typical Cogeneration Results on the CHP Diagram
<table>
<thead>
<tr>
<th></th>
<th>Conventional</th>
<th>Cogeneration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating efficiency</td>
<td>33%</td>
<td>77%</td>
</tr>
<tr>
<td>Heat rate (BTU/kWh)</td>
<td>&gt;10,000</td>
<td>5,000-6,000</td>
</tr>
<tr>
<td>NO\textsubscript{x} emission (lbs of NO\textsubscript{x} / MWh)</td>
<td>4.9</td>
<td>0.167</td>
</tr>
<tr>
<td>CO\textsubscript{2} emission (tons of CO\textsubscript{2} / MWh)</td>
<td>1.06</td>
<td>0.30</td>
</tr>
</tbody>
</table>
Plants in the lower Mississippi River Corridor, Base Case. Flow Rates in Million Tons Per Year
## Some Chemical Complexes in the World

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

<table>
<thead>
<tr>
<th>CO₂ emissions and utilization</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total CO₂ added to atmosphere</td>
<td></td>
</tr>
<tr>
<td>Burning fossil fuels</td>
<td>5,500</td>
</tr>
<tr>
<td>Deforestation</td>
<td>1,600</td>
</tr>
<tr>
<td></td>
<td>IPCC (1995)</td>
</tr>
<tr>
<td>Total worldwide CO₂ from consumption and flaring of fossil fuels</td>
<td>EIA (2002)</td>
</tr>
<tr>
<td>United States</td>
<td>1,526</td>
</tr>
<tr>
<td>China</td>
<td>792</td>
</tr>
<tr>
<td>Russia</td>
<td>440</td>
</tr>
<tr>
<td>Japan</td>
<td>307</td>
</tr>
<tr>
<td>All others</td>
<td>3,258</td>
</tr>
<tr>
<td></td>
<td>Stringer (2001)</td>
</tr>
<tr>
<td>U.S. CO₂ emissions</td>
<td></td>
</tr>
<tr>
<td>Industry</td>
<td>630</td>
</tr>
<tr>
<td>Buildings</td>
<td>524</td>
</tr>
<tr>
<td>Transportation</td>
<td>473</td>
</tr>
<tr>
<td>Total</td>
<td>1,627</td>
</tr>
<tr>
<td></td>
<td>EIA (2001)</td>
</tr>
<tr>
<td>U.S. industry (manufacturing )</td>
<td></td>
</tr>
<tr>
<td>Petroleum, coal products and chemicals</td>
<td>175</td>
</tr>
<tr>
<td></td>
<td>McMahon (1999)</td>
</tr>
<tr>
<td>Chemical and refinery (BP)</td>
<td></td>
</tr>
<tr>
<td>Combustion and flaring</td>
<td>97%</td>
</tr>
<tr>
<td>Noncombustion direct CO₂ emission</td>
<td>3%</td>
</tr>
<tr>
<td></td>
<td>Hertwig et al. (2002)</td>
</tr>
<tr>
<td>Agricultural chemical complex in the lower Mississippi River corridor excess high purity CO₂</td>
<td>0.183</td>
</tr>
<tr>
<td></td>
<td>Arakawa et al. (2001)</td>
</tr>
<tr>
<td>CO₂ used in chemical synthesis</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Commercial Uses of CO$_2$

- 110 million tons of CO$_2$ for chemical synthesis
  - Urea (chiefly, 90 million ton of CO$_2$)
  - Methanol (1.7 million tons of CO$_2$)
  - Polycarbonates
  - Cyclic carbonates
  - Salicylic acid
  - Metal carbonates
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-: Carbamio esters
  - NCO: isocyanates
  - N-C(O)-N: Ureas
- Use as a solvent
- Energy rich products
  - CO, CH₃OH

From Creutz and Fujita, 2000
### Catalytic Reactions of CO₂ from Various Sources

#### Hydrogenation
- \( \text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \) \hspace{0.5cm} \text{methanol}
- \( 2\text{CO}_2 + 6\text{H}_2 \rightarrow \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \) \hspace{0.5cm} \text{ethanol}
- \( \text{CO}_2 + \text{H}_2 \rightarrow \text{CH}_3\text{-O-CH}_3 \) \hspace{0.5cm} \text{dimethyl ether}

#### Hydrolysis and Photocatalytic Reduction
- \( \text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{O}_2 \)
- \( \text{CO}_2 + \text{H}_2 \rightarrow \text{HC=O-OH} + \frac{1}{2}\text{O}_2 \)
- \( \text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_4 + 2\text{O}_2 \)

#### Hydrocarbon Synthesis
- \( \text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \) \hspace{0.5cm} \text{methane and higher HC}
- \( 2\text{CO}_2 + 6\text{H}_2 \rightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O} \) \hspace{0.5cm} \text{ethylene and higher olefins}

#### Carboxylic Acid Synthesis
- \( \text{CO}_2 + \text{H}_2 \rightarrow \text{HC=O-OH} \) \hspace{0.5cm} \text{formic acid}
- \( \text{CO}_2 + \text{CH}_4 \rightarrow \text{CH}_3\text{-C=O-OH} \) \hspace{0.5cm} \text{acetic acid}

#### Other Reactions
- \( \text{CO}_2 + \text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_6 + \text{H}_2 + \text{CO} \) \hspace{0.5cm} \text{dehydrogenation of propane}
- \( \text{CO}_2 + \text{CH}_4 \rightarrow 2\text{CO} + \text{H}_2 \) \hspace{0.5cm} \text{reforming}

#### Graphite Synthesis
- \( \text{CO}_2 + \text{H}_2 \rightarrow \text{C} + \text{H}_2\text{O} \)
- \( \text{CH}_4 \rightarrow \text{C} + \text{H}_2 \)
- \( \text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \)

#### Amine Synthesis
- \( \text{CO}_2 + 3\text{H}_2 + \text{NH}_3 \rightarrow \text{CH}_3\text{-NH}_2 + 2\text{H}_2\text{O} \) \hspace{0.5cm} \text{methyl amine and higher amines}
Application of the System to Chemical Complex in the Lower Mississippi River Corridor

- Base case
- Superstructure
- Optimal structure
Plants in the lower Mississippi River Corridor, Base Case. Flow Rates in Million Tons Per Year
## Processes in the Superstructure

<table>
<thead>
<tr>
<th>Processes in Superstructure</th>
<th>Processes in Base Case</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Processes in Base Case</strong></td>
<td>Electric furnace process for phosphoric acid</td>
</tr>
<tr>
<td>Ammonia</td>
<td>HCl process for phosphoric acid</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>Ammonium sulfate</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>SO₂ recovery from gypsum process</td>
</tr>
<tr>
<td>Urea</td>
<td>S &amp; SO₂ recovery from gypsum process</td>
</tr>
<tr>
<td>UAN</td>
<td>Acetic acid – new CO2-CH4 catalytic process</td>
</tr>
<tr>
<td>Methanol</td>
<td></td>
</tr>
<tr>
<td>Granular triple super phosphate</td>
<td></td>
</tr>
<tr>
<td>MAP &amp; DAP</td>
<td></td>
</tr>
<tr>
<td>Power generation</td>
<td></td>
</tr>
<tr>
<td>Contact process for Sulfuric acid</td>
<td></td>
</tr>
<tr>
<td>Wet process for phosphoric acid</td>
<td></td>
</tr>
<tr>
<td>Acetic acid-conventional process</td>
<td></td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Raw Materials</th>
<th>Cost ($/mt)</th>
<th>Raw Materials</th>
<th>Cost ($/mt)</th>
<th>Products</th>
<th>Price ($/mt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Gas</td>
<td>245</td>
<td>Market cost for short term</td>
<td></td>
<td>Ammonia</td>
<td>190</td>
</tr>
<tr>
<td>Phosphate Rock</td>
<td></td>
<td>purchase</td>
<td></td>
<td>Methanol</td>
<td>96</td>
</tr>
<tr>
<td>wet process</td>
<td>27</td>
<td>Reducing gas</td>
<td>1394</td>
<td>Acetic Acid</td>
<td>623</td>
</tr>
<tr>
<td>electrofurnace</td>
<td>24</td>
<td>Wood gas</td>
<td>634</td>
<td>GTSP</td>
<td>142</td>
</tr>
<tr>
<td>HCl process</td>
<td>25</td>
<td>Sustainable Costs and Credits</td>
<td></td>
<td>MAP</td>
<td>180</td>
</tr>
<tr>
<td>GTSP process</td>
<td>30</td>
<td>Credit for CO₂</td>
<td>6.50</td>
<td>DAP</td>
<td>165</td>
</tr>
<tr>
<td>HCl</td>
<td>50</td>
<td>Consumption</td>
<td></td>
<td>NH₄NO₃</td>
<td>153</td>
</tr>
<tr>
<td>Sulfur</td>
<td></td>
<td>Debit for CO₂</td>
<td>3.25</td>
<td>UAN</td>
<td>112</td>
</tr>
<tr>
<td>Frasch</td>
<td>42</td>
<td>Production</td>
<td></td>
<td>Urea</td>
<td>154</td>
</tr>
<tr>
<td>Claus</td>
<td>38</td>
<td>Credit for HP Steam</td>
<td>10</td>
<td>H₃PO₄</td>
<td>320</td>
</tr>
<tr>
<td>C electrofurnace</td>
<td>760</td>
<td>Credit for IP Steam</td>
<td>6.4</td>
<td>(NH₄)₂SO₄</td>
<td>187</td>
</tr>
</tbody>
</table>

Credit for gypsum          5
Consumption
Debit for gypsum         2.5
Production
Debit for NOₓ           1025
Production
Optimal Structure

- Clay settling ponds (clay, P2O5)
- Tailings (sand)
- Rock slurry
- Slurry water
- Beneficiation plant
- Rainwater
- 100's of evaporated
- Decant water
- Evaporated water
- Gypsum
- Gypsum Stack
- Slurred gypsum
- Old mines (sand)
- Slurried gypsum
- Phosphoric acid plant
- Rock vapor
- Granular
- Triple Super Phosphate
- BFW 4.4765
- Sulfuric acid 0.3266
- Blowdown 2.2255
- H2O 0.5596
- Power generation 0.6581
- NH3 0.5224
- CO2 0.7529
- Natural gas 0.2744
- CO2 0.0938
- Purge 0.0120
- Other use 2.6524
- H2SO4 0.9763
- NH3 0.3341
- Acetic acid plant 0.0082
- Acetic acid
- Methanol plant 0.0022
- H2SO4 1.2958
- Ammonium sulfate 0.0146
## Comparison of Base Case and Optimal Structure

<table>
<thead>
<tr>
<th></th>
<th>Base case</th>
<th>Optimal structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Profit (U.S.$/year)</td>
<td>148,087,243</td>
<td>246,927,825</td>
</tr>
<tr>
<td>Environmental cost (U.S.$/year)</td>
<td>179,481,000</td>
<td>123,352,900</td>
</tr>
<tr>
<td>Sustainability cost (U.S.$/year)</td>
<td>-17,780,800 energy</td>
<td>-16,148,900 energy</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>329,030-658,061</td>
<td>647,834</td>
<td>658,061</td>
<td>3,834</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>0-178,547</td>
<td>178,525</td>
<td>89,262</td>
<td>-324</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>113,398-226,796</td>
<td>226,796</td>
<td>113,398</td>
<td>26</td>
</tr>
<tr>
<td>Urea</td>
<td>49,895-99,790</td>
<td>99,790</td>
<td>49,895</td>
<td>63</td>
</tr>
<tr>
<td>Methanol</td>
<td>90,718-181,437</td>
<td>90,719</td>
<td>90,719</td>
<td>1,083</td>
</tr>
<tr>
<td>UAN</td>
<td>30,240-60,480</td>
<td>60,480</td>
<td>60,480</td>
<td>0</td>
</tr>
<tr>
<td>MAP</td>
<td>0-321,920</td>
<td>321,912</td>
<td>160,959</td>
<td></td>
</tr>
<tr>
<td>DAP</td>
<td>0-2,062,100</td>
<td>2,062,100</td>
<td>1,031,071</td>
<td>1,063</td>
</tr>
<tr>
<td>GTSP</td>
<td>0-822,300</td>
<td>822,284</td>
<td>411,150</td>
<td>518</td>
</tr>
<tr>
<td>Contact process sulfuric acid</td>
<td>1,851,186-3,702,372</td>
<td>3,702,297</td>
<td>2,812,817</td>
<td>-11,368</td>
</tr>
<tr>
<td>Wet process phosphoric acid</td>
<td>697,489-1,394,978</td>
<td>1,394,950</td>
<td>697,489</td>
<td>3,702</td>
</tr>
<tr>
<td>Electric furnace phosphoric acid</td>
<td>697,489-1,394,978</td>
<td>na</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>HCl to phosphoric acid</td>
<td>697,489-1,394,978</td>
<td>na</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ammonium sulfate</td>
<td>0-2,839,000</td>
<td>na</td>
<td>1,295,770</td>
<td>726</td>
</tr>
<tr>
<td>Acetic acid (standard)</td>
<td>0-8,165</td>
<td>8,165</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Acetic acid (new)</td>
<td>0-8,165</td>
<td>na</td>
<td>8,165</td>
<td>92</td>
</tr>
<tr>
<td>SO2 recovery from gypsum</td>
<td>0-1,804,417</td>
<td>na</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>S &amp; SO2 recovery from gypsum</td>
<td>0-903,053</td>
<td>na</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ammonia sale</td>
<td>0</td>
<td></td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ammonium Nitrate sale</td>
<td>218,441</td>
<td></td>
<td>105,043</td>
<td></td>
</tr>
<tr>
<td>Urea sale</td>
<td>39,076</td>
<td></td>
<td>3,223</td>
<td></td>
</tr>
<tr>
<td>Wet process phosphoric acid sale</td>
<td>13,950</td>
<td></td>
<td>6,975</td>
<td></td>
</tr>
<tr>
<td>Methanol sale</td>
<td>86,361</td>
<td></td>
<td>90,719</td>
<td></td>
</tr>
<tr>
<td>Total energy requirement from fuel gas</td>
<td>2,912</td>
<td></td>
<td>1,344</td>
<td></td>
</tr>
</tbody>
</table>
## Comparison of Acetic Acid Processes

<table>
<thead>
<tr>
<th></th>
<th>Conventional Process</th>
<th>New Catalytic Process</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Raw Materials</strong></td>
<td>Methanol, Carbon Monoxide</td>
<td>Methane, Carbon Dioxide</td>
</tr>
<tr>
<td><strong>Reaction Condition</strong></td>
<td>450K, 30bar</td>
<td>350K, 25bar</td>
</tr>
<tr>
<td><strong>Conversion of methane</strong></td>
<td>100%</td>
<td>97%</td>
</tr>
<tr>
<td><strong>Equipment</strong></td>
<td>reactor, flash drum, four distillation columns</td>
<td>reactor, distillation column</td>
</tr>
</tbody>
</table>
# Production Costs for Acetic Acid

Moulijn, et al., 2001

<table>
<thead>
<tr>
<th>Plant Production Cost, (cents per kg)</th>
<th>Methanol Carbon Monoxide</th>
<th>Methane Carbon Dioxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw materials</td>
<td>21.6</td>
<td>21.6</td>
</tr>
<tr>
<td>Utilities</td>
<td>3.3</td>
<td>1.7</td>
</tr>
<tr>
<td>Labor</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Other (capital, catalyst)</td>
<td>10.1</td>
<td>10.1</td>
</tr>
<tr>
<td>Total Production Cost</td>
<td>36.2</td>
<td>34.6</td>
</tr>
</tbody>
</table>

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 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
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 HYSYS 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

On-Line Optimization

Fig. 1 Overview of Advanced Process Analysis System
On-Line Optimization

Gross Error Detection and Data Reconciliation

Optimization Algorithm
Economic Model
Plant Model

setpoints for controllers
plant measurements

Distributed Control System

sampled plant data

Gross Error Detection and Data Reconciliation

reconciled plant data

optimall operating conditions
setpoint targets

Optimization Algorithm Economic Model Plant Model

updated plant parameters

Parameter Estimation

economic model parameters
Reactor Analysis

Reactor Type

Homogeneous
- Gas Phase
  - PFR, CSTR, Batch Reactors

Liquid Phase

Heterogeneous
- Gas-Liquid
  - CSTR Bubble Reactor
  - Packed Bed

Catalytic
- Gas
  - Fixed Bed
  - Trickle Bed
- Liquid
  - Fluidised Bed Reactors
  - Bubble Slurry
- Gas-Liquid
  - 3-Phase Fluidised Bed
Energy Integration – Pinch Analysis
Pollution Assessment

Waste Reduction Algorithm (WAR) and Environmental Impact Theory

Pollution Index

\[ I = \frac{- (\sum Out + \sum Fugitive)}{\sum P_n} \]

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 NO\textsubscript{x} and CO\textsubscript{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
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