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

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New, energy-efficient and environmentally-acceptable, catalytic processes have been identified that can use excess high purity carbon dioxide as a raw material available in a chemical production complex. The chemical production complex in the lower Mississippi River Corridor has been used to show how these new plants can be integrated into this existing infrastructure using the Chemical Complex and Cogeneration Analysis System. Laboratory and pilot plant experiments were reviewed that describe new methods and catalysts to use carbon dioxide for producing commercially important products. A methodology for selecting the new energy-efficient processes was developed. The selection criteria included operating conditions, energy requirement for reactions, ΔHE and equilibrium conversion based on Gibbs free energy, ΔGE and thermodynamic feasibility of the reactions, catalyst conversion and selectivity, cost and life (time on stream to deactivation) and methods to regenerate catalysts. Also included were demand and potential sales of products and market penetration. In addition, cost of raw materials, energy, environmental, sustainable and other manufacturing costs were evaluated along with hydrogen consumption for hydrogenation reactions. Based on the methodology for selecting new processes, twenty potential processes were identified as candidates for new energy efficient and environmentally-acceptable plants. These processes were simulated using HYSYS and a value-added economic analysis was evaluated for each process. They included production of methanol, ethanol, DME, propylene, formic acid, acetic acid, styrene, methylamines, graphite and synthesis gas. A base case of existing plants in a chemical production complex in the lower Mississippi river corridor was developed that included thirteen multiple plant production units plus associated utilities for power, steam and cooling water and facilities for waste treatment. The System was used with the base case and potentially new plants for carbon dioxide and an optimal configuration of plants was determined for three different case studies. Typical results showed that the profit increased by 40%, environmental costs increased by 4.5% and sustainable costs decreased by 17% compared to the base case of existing plants. These results illustrated the capability of the Chemical Complex and Cogeneration Analysis System to select an optimum configuration of plants in a chemical production complex and incorporate economic, environmental and sustainable costs. These results are typical of what can be expected from applying the System to existing chemical production complexes worldwide. The Chemical Complex and Cogeneration Analysis System has been developed by industry-university collaboration and the System is available from the LSU Minerals Processing Research Institute's web site www.mpri.lsu.edu at no charge.

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

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Overview of Presentation

- Introduction
- Carbon Dioxide Reactions
- New Process Selection
- Incorporating New Processes in Chemical Complex
- Results
- Conclusions
- Opportunities for the Future

Introduction

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

Pellegrino, DOE chemical IOF report , 2002

Introduction

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

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.

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

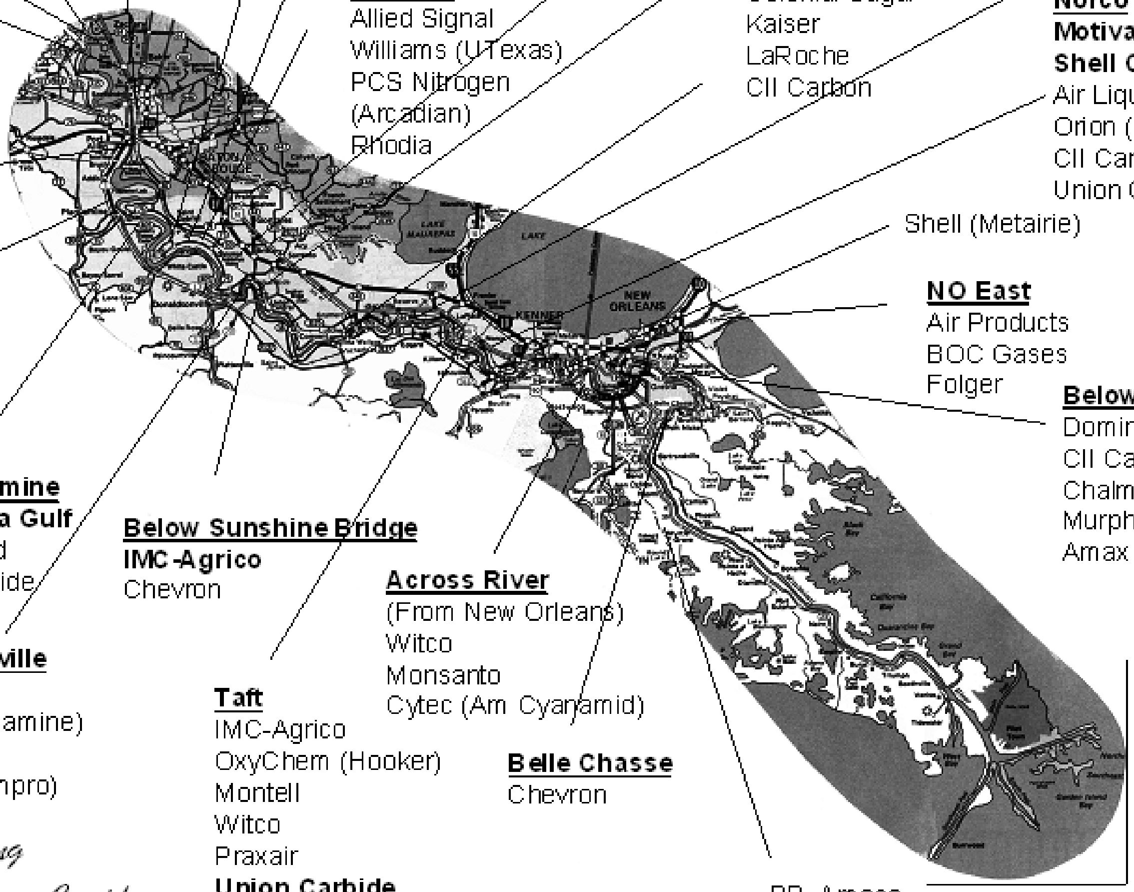
Introduction

- Opportunity
  - Processes for conversion of greenhouse gases to valuable products

- Methodology
  - Chemical Complex Analysis System

  - Application to chemical production complex in the lower Mississippi River corridor

Plants in the lower Mississippi River Corridor



Saint Francisville
Crown Vantage

Port Hudson
Georgia-Pacific

North of Baton Rouge
Ferro (Grant)
Safety - Kleen (Laidlaw)
Exxon (Allied / Paxon)
Exxon Resins
Deltech (Foster Grant)
Exxon Plastics

Baton Rouge
Rhodia (Stauffer)
LaRoche (Kaiser)
DSM (Copolymer
Albemarle (Ethyl)
Formosa (Allied)
Exxon - Refinery
Exxon Chemical
Allied Signal

St Gabriel
Air Products
Novartis (Ciba Geigy)
Ciba
Pioneer (Stauffer)
ICI
Zeneca

Carville
Cosmar
Fina

Geismar
Allied Signal
Williams (UTexas)
PCS Nitrogen
(Arcadian)
Rhodia

Geismar
Borden
Air Liquide
Uniroyal
Rubicon
Praxair
BASF
Shell Chem
Air Prod
Vulcan

Sunshine Bridge & Below
Air Products
Motiva (Star/Texaco)
DuPont
OxyChem (Convent)
IMC - Agrico

Gramercy
Colonial Sugar
Kaiser
LaRoche
CII Carbon

Garyville
Nalco
Marathon
Epsilon
Betz (Reserve)
DuPont (LaPlace)

Norco
Motiva (Shell NMC)
Shell Chemical
Air Liquide
Orion (TransAmerican)
CII Carbon
Union Carbide

Shell (Metairie)

Port Allen
Placid
Exxon - Lubes

Addis / Plaquemine
Borden (OxyChem)
Sid Richardson
DSM Copolymer
Dow
Geon
Air Liquide
Air Products

Plaquemine
Georgia Gulf
Ashland
Air Liquide
Praxair

Donaldsonville
CF
Borden (Melamine)
Triad #1
Triad #2 (Ampro)

Below Sunshine Bridge
IMC-Agrico
Chevron

Taft
IMC-Agrico
OxyChem (Hooker)
Montell
Witco
Praxair
Union Carbide

Across River
(From New Orleans)
Witco
Monsanto
Cytec (Am Cyanamid)

Belle Chasse
Chevron

NO East
Air Products
BOC Gases
Folger

Below NO
Domino Sugar
CII Carbon
Chalmette Ref (Mobil)
Murphy
Amax

BP Amoco

Petrochemical Plants Along
The lower Mississippi River Corridor

Source: Peterson, R.W., 2000

Some Chemical Complexes in the World

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

Some Chemical Complexes in the World (Continued)

- Asia
  - The Singapore petrochemical complex in Jurong Island (Singapore)
  - Petrochemical complex of Daqing Oilfield Company Limited (China)
  - SINOPEC Shanghai Petrochemical Co. Ltd. (China)
  - Joint-venture of SINOPEC and BP in Shanghai under construction (2005) (China)
  - Jamnagar refinery and petrochemical complex (India)
  - Sabic company based in Jubail Industrial City (Saudi Arabia)
  - Petrochemical complex in Yanbu (Saudi Arabia)
  - Equate (Kuwait)
- Africa
  - petrochemical industries complex at Ras El Anouf (Libya)

Carbon Dioxide Emissions

(Million Metric Tons Carbon Equivalent Per Year)

- Total CO_2 added to atmosphere
  - Burning fossil fuels
  - Deforestation 1,600

- Total worldwide CO_2 from consumption and flaring of fossil fuels

  5,500
  - United States 1,526
  - China 792
  - Russia 440
  - Japan
  - All others 3,258

- U.S. CO_2 emissions
  - Industry 630
  - Buildings
  - Transportation 473

  307
  - Total 1,627

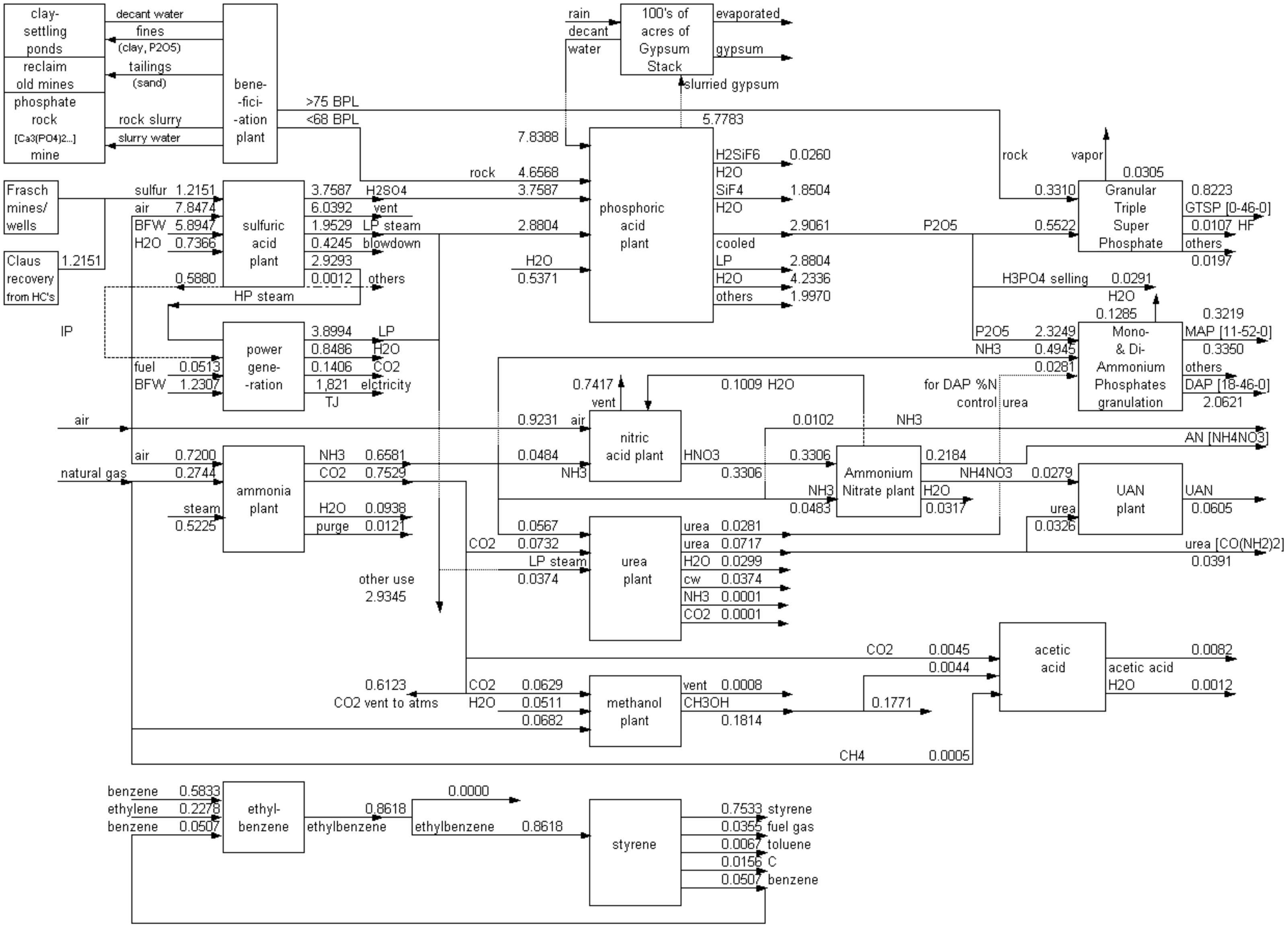
- U.S. industry (manufacturing): Petroleum, coal products and chemicals 175
- Chemical complex in the lower Mississippi River corridor excess high purity CO_2 0.61

Commercial Uses of CO_2

110 million m tons per year 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

Base Case of Existing Plants



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

Surplus Carbon Dioxide

- Ammonia plants produce 0.75 million tons per year in lower Mississippi River corridor.

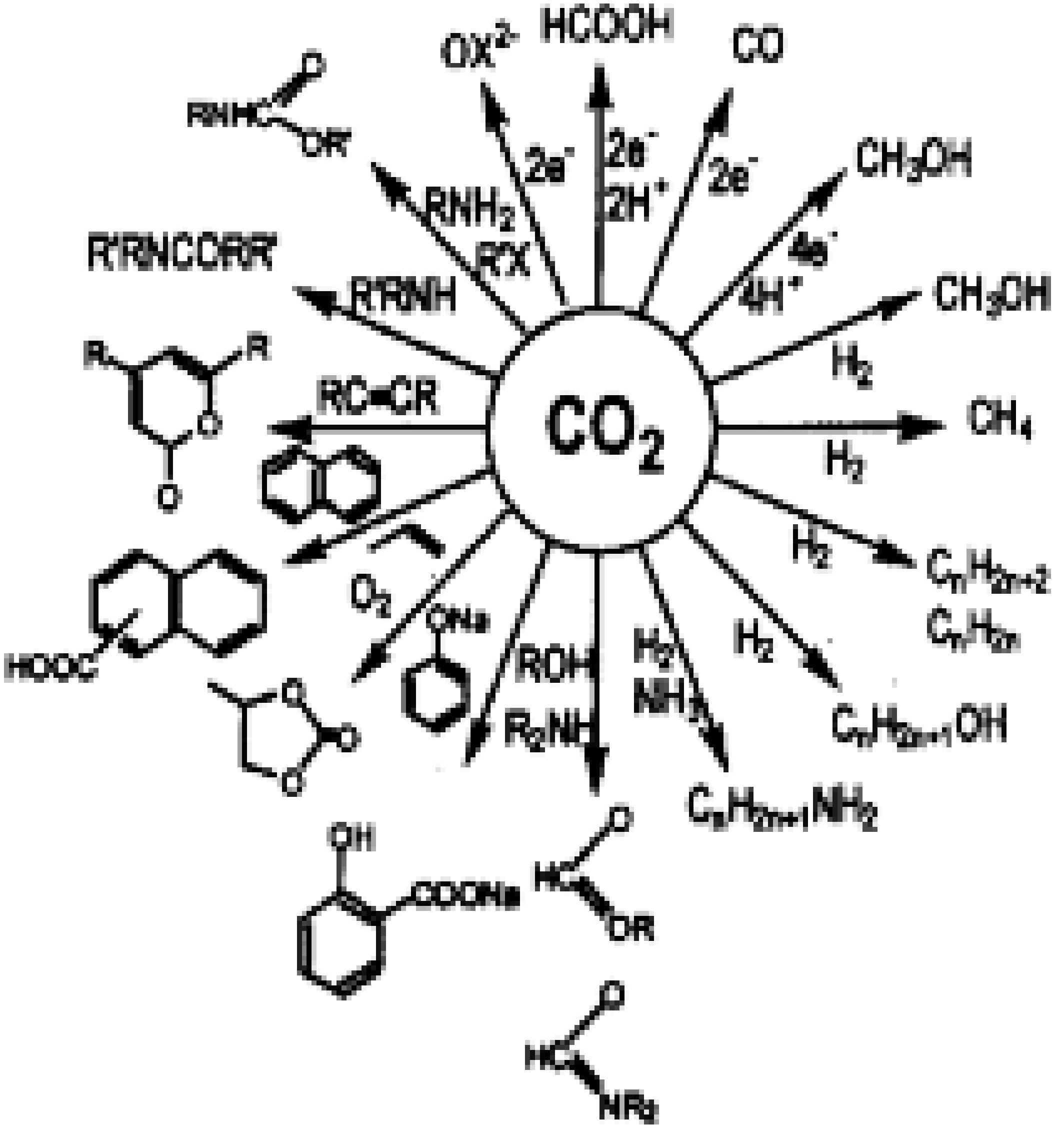
- Methanol and urea plants consume 0.14 million tons per year.

- Surplus high-purity carbon dioxide 0.61 million tons per year vented to atmosphere.

- Plants are connected by CO_2 pipelines.

Greenhouse Gases as Raw Material

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



From Creutz and Fujita, 2000

Catalytic Reactions of CO_2

Hydrogenation

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

Hydrolysis and Photocatalytic Reduction

$CO_2 + 2H_2O \rightarrow CH_3OH + O_2$

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

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

Hydrocarbon Synthesis

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

Carboxylic Acid Synthesis

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

Other Reactions

CO_2 + ethylbenzene →styrene

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

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

Graphite Synthesis

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

Amine Synthesis

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

Methodology of Developing New Carbon Dioxide Processes

- Identify potentially new processes
- Simulate with HYSYS
- Estimate utilities required
- Evaluate value added economic analysis
- Select best processes based on value added economics
- Integrate new processes with existing ones to form a superstructure for optimization

Identifying Potentially New Processes

- Literature review of new experimental studies – five international conferences
- Compare with the existing commercial processes
- Select potentially new processes

Selection Criterion

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

Potential Energy Savings through Improved Catalysts in Trillion BTUs (Pellegrino, 2000)

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

Selected Studies

- Eighty-six experimental studies reviewed
- Seventy experimental studies compared to commercial plants
- Twenty potentially new process selected for evaluation with HYSYS

Selected Studies (Continued)

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

Twenty Processes Selected for HYSYS Design

Chemical	Synthesis Route	Reference
Methanol	CO2 hydrogenation	Nerlov and Chorkendorff, 1999
	CO2 hydrogenation	Toyir, et al., 1998
	CO2 hydrogenation	Ushikoshi, et al., 1998
	CO2 hydrogenation	Jun, et al., 1998
	CO2 hydrogenation	Bonivardi, et al., 1998
Ethanol	CO2 hydrogenation	Inui, 2002
	CO2 hydrogenation	Higuchi, et al., 1998
Dimethyl Ether	CO2 hydrogenation	Jun, et al., 2002
Formic Acid	CO2 hydrogenation	Dinjus, 1998
Acetic Acid	From methane and CO2	Taniguchi, et al., 1998
Styrene	Ethylbenzene dehydrogenation	Sakurai, et al., 2000
	Ethylbenzene dehydrogenation	Mimura, et al., 1998
Methylamines	From CO2, H2, and NH3	Arakawa, 1998
Graphite	Reduction of CO2	Nishiguchi, et al., 1998
Hydrogen/ Synthesis Gas	Methane reforming	Song, et al., 2002
	Methane reforming	Shamsi, 2002
	Methane reforming	Wei, et al., 2002
	Methane reforming	Tomishige, et al., 1998
Propylene	Propane dehydrogenation	Takahara, et al., 1998
	Propane dehydrogenation	C & EN, 2003

HYSYS Simulations

- Based on production capacities of existing plants
- Process design gave:
    - Process flow diagram
    - Energy requirements
    - Stream flow rates

Value Added Economic Model

- Profit = Σ Product Sales – Σ Raw Material Costs
  - Σ Energy Costs

- Product selling prices and raw material costs were obtained from literature
- Steam and cooling water required were specified from the HYSYS PFD
- Stream flow rates obtained from HYSYS PFD

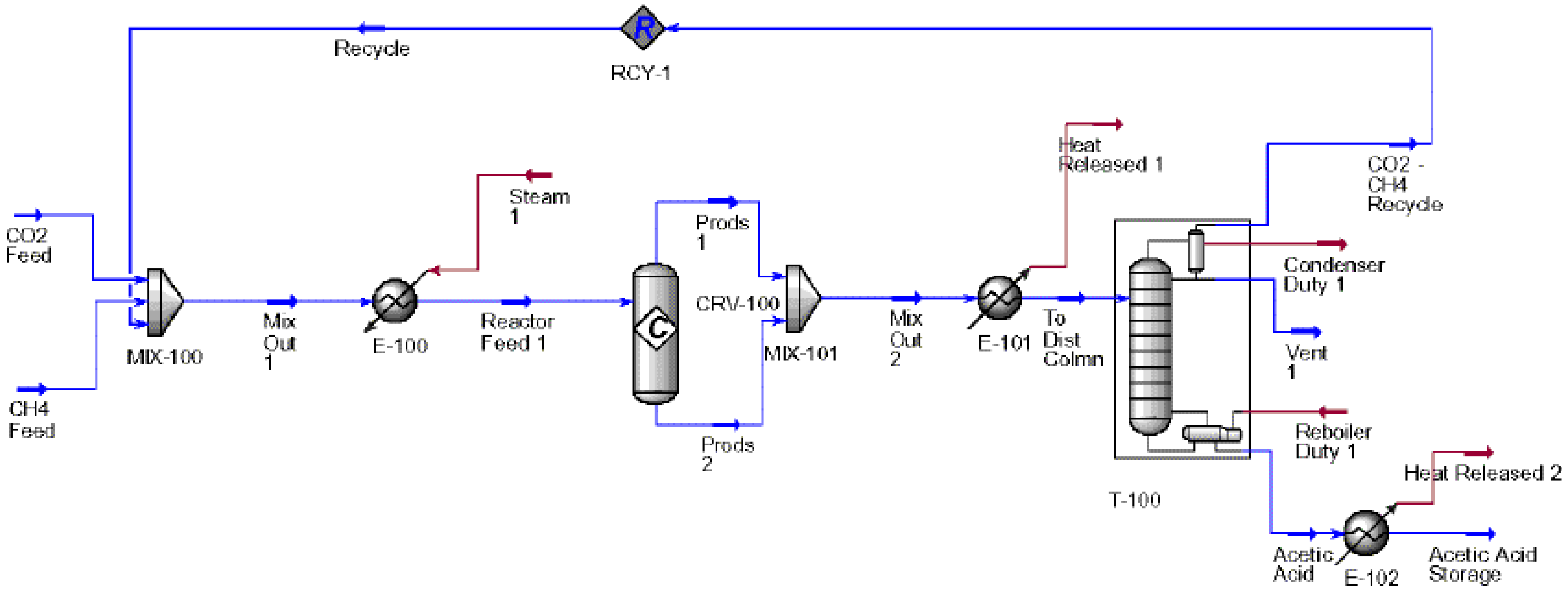
Example: Acetic Acid Process

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

Example: Acetic Acid Process (Continued)

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

HYSYS Process Flow Diagram for Acetic Acid Process



Economic Results for HYSYS Simulated Acetic Acid Process

Product/Raw Material	Flow Rate from HYSYS Simulation (kg/hr)	Cost/Selling Price ($/kg)
Carbon Dioxide	685	0.003
Methane	249	0.172
Acetic Acid	933	1.034
HP Steam	766.0	0.00865
Cooling Water	13,730	6.7×10^{-6}
Value Added Profit	$ 913/hr	98 cents/kg

Integration into Superstructure

- Twenty processes simulated
- Fourteen processes selected based on value added economic model
- Integrated into the superstructure for optimization with the System

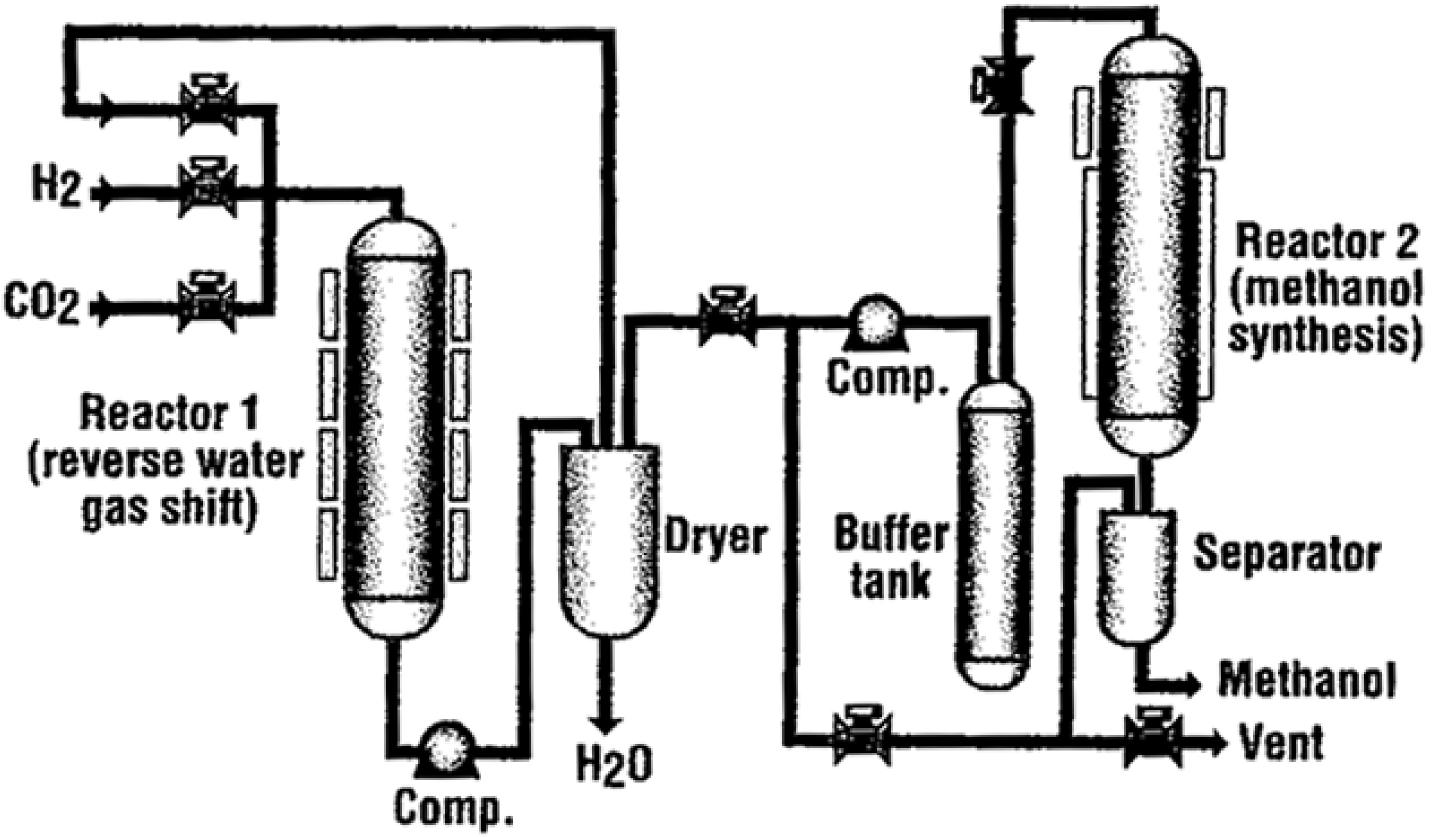
New Processes Included in Complex

Product	Synthesis Route	Value Added Profit (cents/kg)
Methanol	CO_2 hydrogenation	2.8
Methanol	CO_2 hydrogenation	3.3
Methanol	CO_2 hydrogenation	7.6
Methanol	CO_2 hydrogenation	5.9
Ethanol	CO_2 hydrogenation	33.1
Dimethyl Ether	CO_2 hydrogenation	69.6
Formic Acid	CO_2 hydrogenation	64.9
Acetic Acid	From CH_4 and CO_2	97.9
Styrene	Ethylbenzene dehydrogenation	10.9
Methylamines	From CO_2, H_2, and NH_3	124
Graphite	Reduction of CO_2	65.6
Synthesis Gas	Methane reforming	17.2
Propylene	Propane dehydrogenation	4.3
Propylene	Propane dehydrogenation with CO_2	2.5

New Processes Not Included in Complex

Product	Synthesis Route	Value Added Profit (cents/kg)
Methanol	CO2 hydrogenation	-7.6
Ethanol	CO2 hydrogenation	31.6
Styrene	Ethylbenzene dehydrogenation	4.5
Synthesis Gas	Methane reforming	17.2
Synthesis Gas	Methane reforming	17.1
Synthesis Gas	Methane reforming	17.1

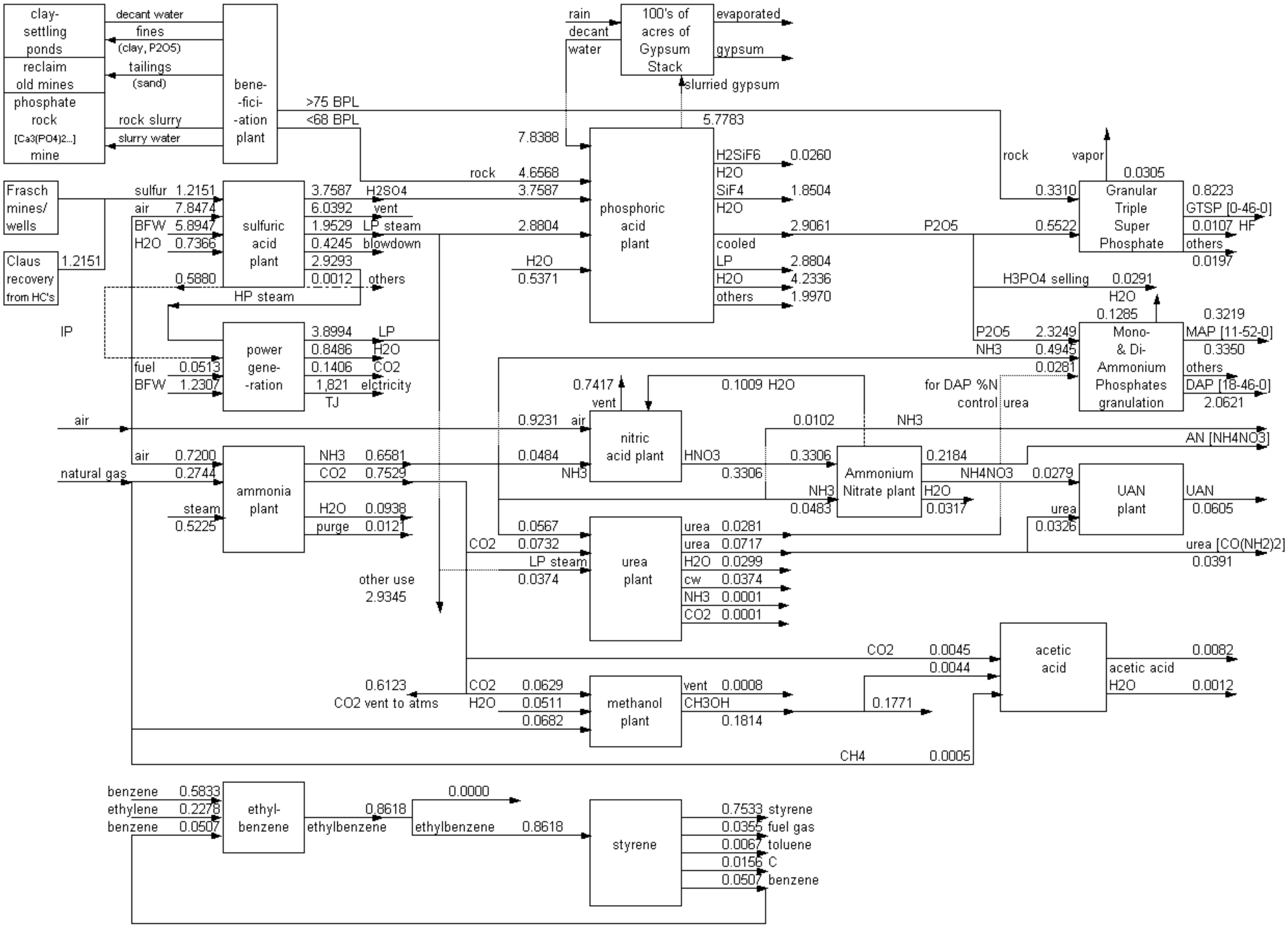
Korea Institute of Science and Technology (KIST) operating a 100 kg/day methanol pilot plant since April 2002 using CO_2



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

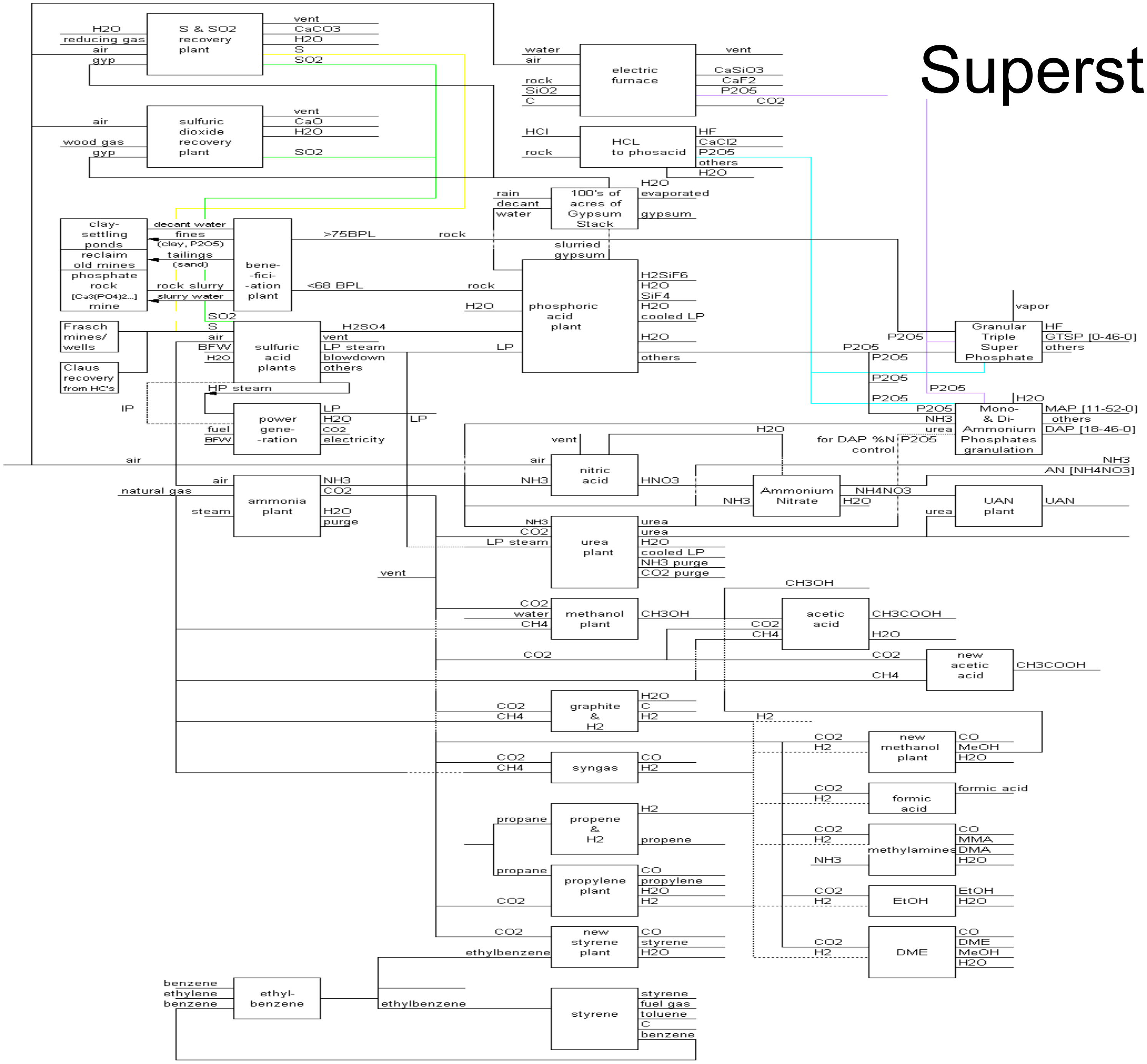
- Base case
- Superstructure
- Optimal structure

Base Case of Existing Plants



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

Superstructure



Processes in the Superstructure

Plants in the Base Case

- Ammonia
- Nitric acid
- Ammonium nitrate
- Urea
- UAN
- Methanol
- Granular triple super phosphate
- MAP and DAP
- Sulfuric acid
- Phosphoric acid
- Acetic acid
- Ethylbenzene
- Styrene

Plants Added to form the Superstructure

- Acetic acid from CO_2 and CH_4
- Graphite and H_2
- Syngas from CO_2 and CH_4
- Propane dehydrogenation
- Propylene from propane and CO_2
- Styrene from ethylbenzene and CO_2
- Methanol from CO_2 and H_2 (4)
- Formic acid
- Methylamines
- Ethanol
- Dimethyl ether
- Electric furnace phosphoric acid
- HCl process for phosphoric acid
- SO_2 recovery from gypsum
- S and SO_2 recovery from gypsum

Superstructure Characteristics

Options

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

Mixed Integer Nonlinear Program

843	continuous variables
23	integer variables
777	equality constraint equations for material and energy balances
64	inequality constraints for availability of raw materials demand for product, capacities of the plants in the complex

Some of the Raw Material Costs, Product Prices and Sustainability Cost and Credits

Raw Materials	Cost ($/mt)
Natural gas	235
Phosphate rock	
Wet process	27
Electro-furnace	34
Haifa process	34
GTSP process	32
HCl	95
Sulfur	
Frasch	53
Claus	21

Sustainable Cost and Credits	Cost/Credit ($/mt)
Credit for CO2 consumption	6.50
Debit for CO2 production	3.25
Credit for HP Steam	11
Credit for IP Steam	7
Credit for gypsum consumption	5.0
Debit for gypsum production	2.5
Debit for NOx production	1,025
Debit for SO2 production	192

Products	Price ($/mt)
Ammonia	224
Methanol	271
Acetic acid	1,032
GTSP	132
MAP	166
DAP	179
NH4NO3	146
Urea	179
UAN	120
Phosphoric	496

Triple Bottom Line

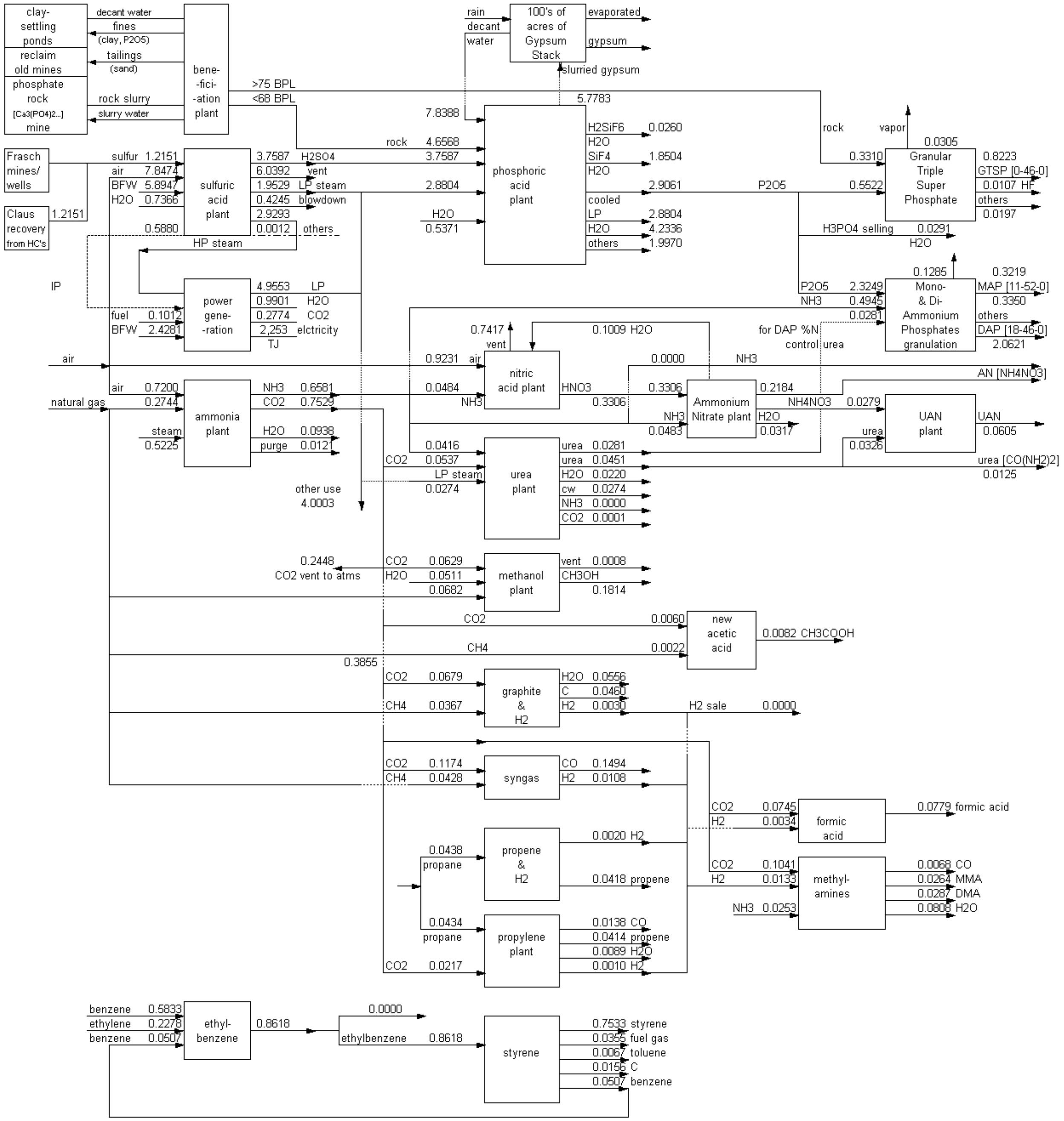
Triple Bottom Line = Σ Product Sales – Σ Raw Material Costs - Σ Energy Costs

-Σ Environmental Costs + Σ Sustainable (Credits – Costs)

Triple Bottom Line = Profit - Σ Environmental Costs

+ Σ Sustainable (Credits – Costs)

Optimal Structure



Plants in the Optimal Structure from the Superstructure

Existing Plants in the Optimal Structure	New Plants in the Optimal Structure
Ammonia	Formic acid
Nitric acid	Acetic acid – new process
Ammonium nitrate	Methylamines
Urea	Graphite
UAN	Hydrogen/Synthesis gas
Methanol	Propylene from CO_2
Granular triple super phosphate (GTSP)	Propylene from propane dehydrogenation
MAP & DAP	
Power generation	New Plants Not in the Optimal Structure
Contact process for Sulfuric acid	Electric furnace process for phosphoric acid
Wet process for phosphoric acid	HCl process for phosphoric acid
Ethylbenzene	SO_2 recovery from gypsum process
Styrene	S & SO_2 recovery from gypsum process
	Methanol - Bonivardi, et al., 1998
Existing Plants Not in the Optimal Structure	Methanol – Jun, et al., 1998
	Methanol – Ushikoshi, et al., 1998
Acetic acid	Methanol – Nerlov and Chorkendorff, 1999
	Ethanol
	Dimethyl ether
	Styrene - new process

Sales and Costs Associated with the Triple Bottom Line for the Base Case and Optimal Structure

	Base Case million dollars/year	Optimal Structure million dollars/year
Income from Sales	1,316	1,544
Economic Costs (Raw Materials and Utilities)	560	606
Raw Material Costs	548	582
Utility Costs	12	24
Environmental Cost (67% of Raw Material Cost)	365	388
Sustainable Credits (+)/Costs (-)	21	24
Triple Bottom Line	412	574

Carbon Dioxide Consumption in Bases Case and Optimal Structure

	Base Case million metric tons/year	Optimal Structure million metric tons/year
CO_2 produced by NH_3 plant	0.75	0.75
CO_2 consumed by methanol, urea and other plants	0.14	0.51
CO_2 vented to atmosphere	0.61	0.24

Comparison of Capacities for the Base Case and Optimal Structure

Plant name	Capacity (upper-lower bounds) (mt/year)	Base Case Capacity (mt/year)	Energy Requirement (TJ/year)	Optimal Capacity (mt/year)	Energy Requirement (TJ/year)
Ammonia	329,000-658,000	658,000	3,820	658,000	3,820
Nitric acid	89,300-179,000	179,000	-648	179,000	-648
Ammonium nitrate	113,400-227,000	227,000	117	227,000	117
Urea	49,900-99,800	99,800	128	73,200	94
Methanol	90,700-181,400	181,400	2,165	181,400	2,165
UAN	30,200-60,500	60,500	0	60,500	0
MAP	161,000-322,000	322,000	2,137	322,000	2,137
DAP	1,031,050-2,062,100	2,062,100		2,062,100	
GTSP	411,150-822,300	822,300	1,036	822,300	1,036
Contact process sulfuric acid	1,850,000-3,703,000	3,703,000	-14,960	3,703,000	-14,960
Wet process phosphoric acid	697,500-1,395,000	1,395,000	7,400	1,395,000	7,400
Ethylbenzene	430,900-861,800	861,800	-755	861,800	-755
Styrene	385,500-771,000	753,300	3,318	753,200	3,318
Acetic acid	4,080-8,170	8,170	268	0	0

CO_2 vented		612,300		244,800	
Total energy requirement			4,026		7,658

Extensions to Optimal Complex

	Base Case million dollars/year	Optimal million dollars/year	Use all CO_2 million dollars/year	Max NH_3 Plant million dollars/year	Equal Credit and Debit for CO_2 million dollars/year
Income from Sales	1,316	1,544	1,392	1,212	1,544
Economic Costs (Raw Materials and Utilities)	560	606	551	464	606
Raw Material Costs	548	582	525	440	582
Utility Cost	12	24	26	24	24
Environmental Cost (67% of Raw Material Cost)	365	388	350	294	388
Sustainable Credits (+)/Costs (-)	21	24	19	27	22
Triple Bottom Line	412	574	509	481	572
	million mtons/year	million mtons/year	million mtons/year	million mtons/year	million mtons/year
CO_2 produced by NH_3 Plant	0.75	0.75	0.56	0.75	0.75
CO_2 consumed by methanol, urea and other plants	0.14	0.52	0.	0.75	0.52
CO_2 vented to atmosphere	0.61	0.24	0.0	0.0	0.24

Multicriteria Optimization

max: P= Σ Product Sales - Σ Economic Costs - Σ Environmental Costs

S = Σ Sustainable (Credits – Costs)

subject to: Multi-plant material and energy balances
Product demand, raw material availability, plant capacities

Efficient or Pareto Optimal Solutions

Optimal points where attempting to improving the value of one objective would cause another objective to decrease.

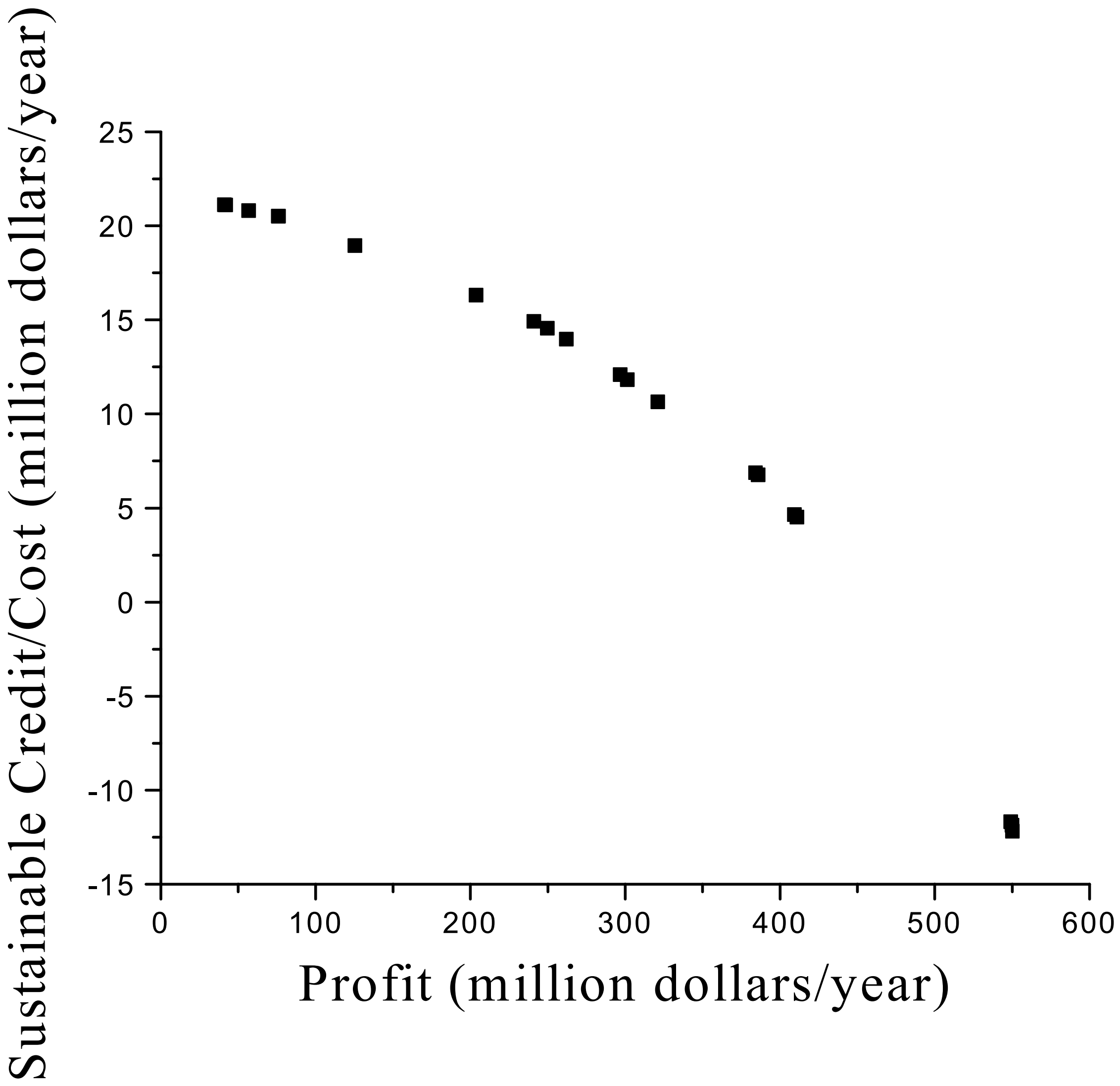
Multicriteria Optimization

Convert to a single criterion optimization problem

max: $w_1P + w_2 S$

subject to: Multi-plant material and energy balances
Product demand, raw material availability,
plant capacities

Multicriteria Optimization



Monte Carlo Simulation

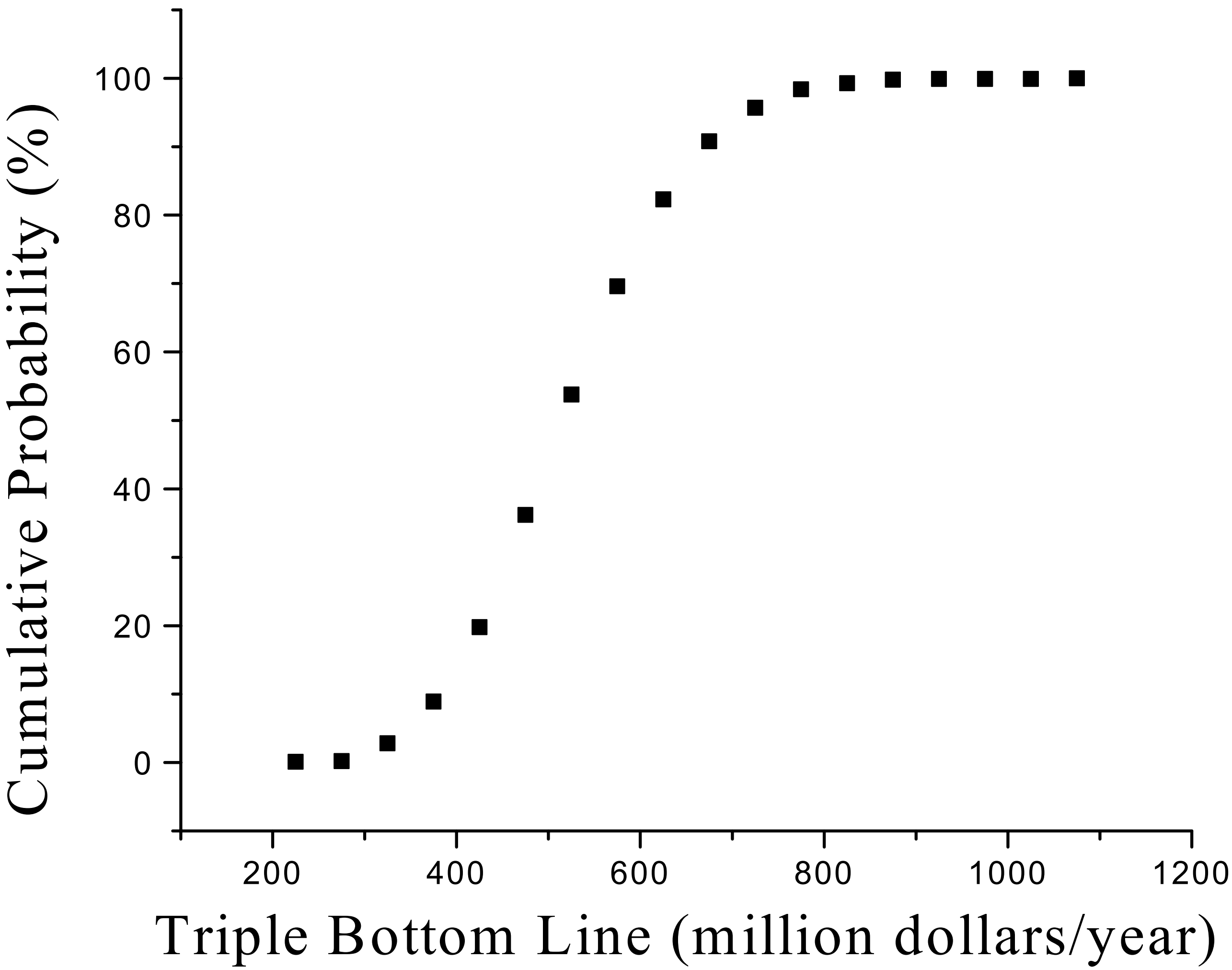
Used to determine the sensitivity of the optimal solution to the costs and prices used in the chemical production complex economic model.

A result is the cumulative probability distribution,
a curve of the probability as a function of the triple bottom line.

A value of the cumulative probability for a given value of the triple bottom line is the probability that the triple bottom line will be equal to or less that value.

This curve is used to determine the upside and downside risks

Monte Carlo Simulation



Conclusions

Fourteen new energy-efficient and environmentally acceptable catalytic processes have been identified that can use excess high purity carbon dioxide as a raw material

The optimum configuration of plants was determined based on economic, environmental and sustainable costs using the Chemical Complex Analysis System.

Seven potentially new processes in the optimal structure acetic acid, graphite, formic acid, methylamines, propylene (2) and synthesis gas production.

Triple bottom line increased from $412 to $574 million per year

Energy increased from 4,030 to 7,660 TJ/year.

Conclusions

Multcriteria optimization determines the best values of competing objectives

Monte Carlo simulation provides a statistical basis for sensitivity analysis of prices and costs

Chemical Complex Analysis System

- Gives corporate engineering groups new capability to design:

  New processes for products from greenhouse gases

  Energy efficient and environmentally acceptable plants

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Future Research

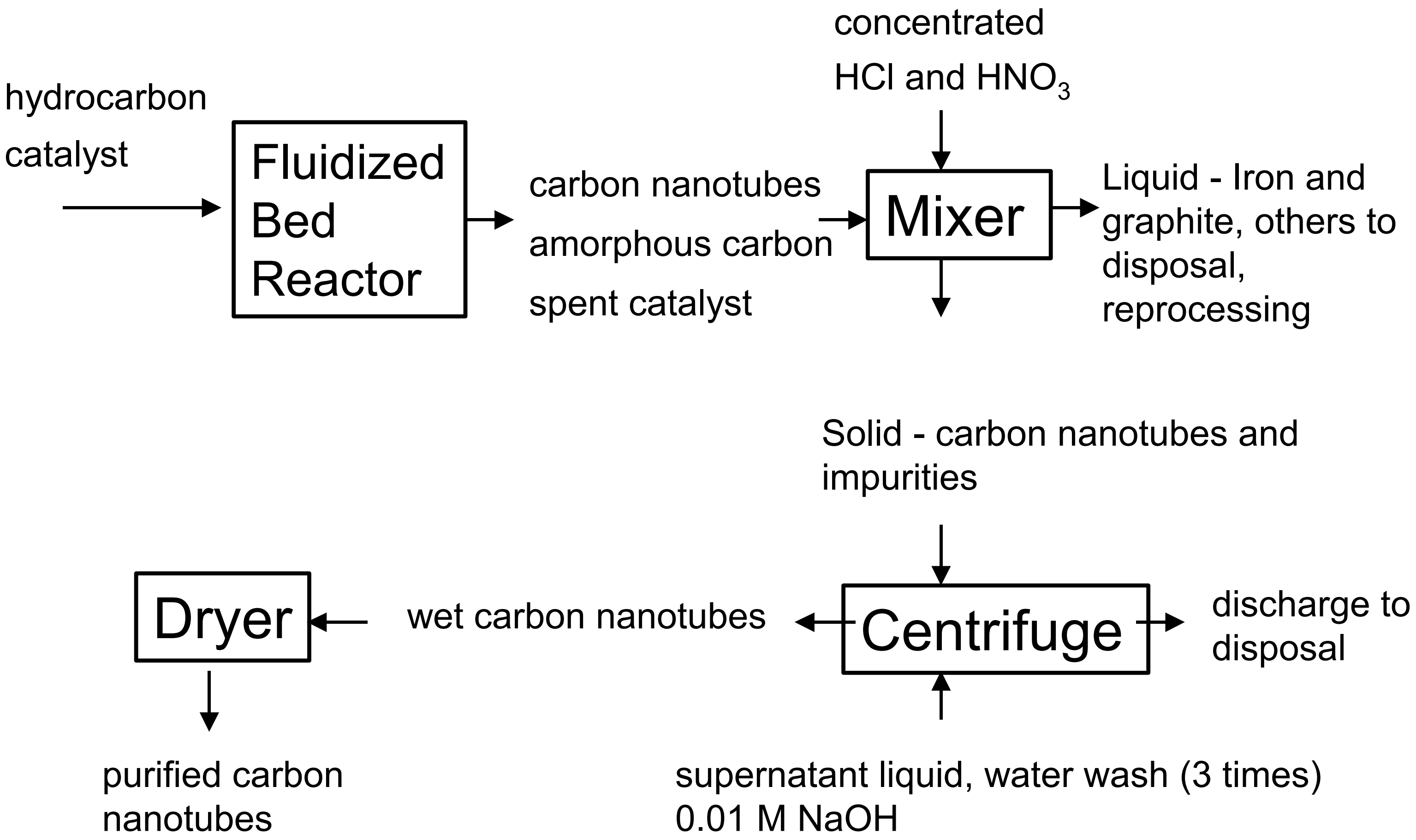
Methodology can be applied to other sources of carbon dioxide such as flue gases from power plants

Potential processes for fullerines and carbon nanotubes can be designed based on laboratory experimental studies that are available in the literature as was done for carbon dioxide.

Laboratory catalytic reactors are used to produce gram quantities of carbon nanotubes, and batch purification involves removing impurities with strong mineral acids.

These potentially new processes are high temperature, energy intensive and generate hazardous and toxic wastes

Future Research



hydrocarbon

catalyst

Fluidized Bed Reactor

carbon nanotubes

amorphous carbon

spent catalyst

concentrated

HCl and HNO_3

Mixer

Liquid - Iron and graphite, others to disposal, reprocessing

Solid - carbon nanotubes and impurities

Centrifuge

discharge to disposal

supernatant liquid, water wash (3 times)
0.01 M NaOH

wet carbon nanotubes

Dryer

purified carbon nanotubes

Future Research

Summary of Reactor Types Catalysts, Reactants and Operating Conditions Used in Laboratory Synthesis of Carbon Nanotubes

Reactor types: fluidized bed, chemical vapor deposition (packed bed), two-stage furnace, plasma (arc process), laser ablation, electrolysis in molten LiCl

Catalysts: metal catalysts (Co, Ni, Fe, Pt and Pd) deposited on substrates such as silicon, graphite or silica) ferocene, cobaltocene, nickelocene, iron pentacarbonyl, metal oxides

Hydrocarbon reactants: methane, ethylene, benzene, acetylene, naphthalene, xylene, carbon monoxide, ethanol

Reactor temperatures: 650 – 1,200 ^{o}C for fluidized bed, 2,000-3,000 ^{o}C for plasma

Reactor pressures: 1.0 – 50 atms.

Thank you for your attention