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Development and integration of new processes consuming carbon dioxide in multi-plant chemical production complexes

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Abstract Fourteen 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 complex in the lower Mississippi River Corridor was used to show how these new plants could be integrated into this existing infrastructure using the chemical complex analysis system. Eighty-six published articles of laboratory and pilot plant experiments were reviewed that describe new methods and catalysts to use carbon dioxide for producing commercially important products. A methodology for selecting the new energy-efficient processes was developed based on process operating conditions, energy requirements, catalysts, product demand and revenue, market penetration and economic, environmental and sustainable costs. Based on the methodology for selecting new processes, 20 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. From these, 14 of the most promising were integrated in a superstructure that included plants in the existing chemical production complex in the lower Mississippi River corridor (base case). The optimum configuration of plants was determined based on the triple bottom line that includes sales, economic, environmental and sustainable costs using the chemical complex analysis system. From 18 new processes in the superstructure, the optimum structure had seven new processes including acetic acid, graphite,

formic acid, methylamines, propylene and synthesis gas production. With the additional plants in the optimal structure the triple bottom line increased from \$343 million per year to \$506 million per year and energy use increased from 2,150 TJ/year to 5,791 TJ/year. Multi-criteria optimization has been used with Monte Carlo simulation to determine the sensitivity of prices, costs, and sustainability credits/cost to the optimal structure of a chemical production complex. In essence, for each Pareto optimal solution, there is a cumulative probability distribution function that is the probability as a function of the triple bottom line. This information provides a quantitative assessment of the optimum profit versus sustainable credits/cost, and the risk (probability) that the triple bottom line will meet expectations. The capabilities of the chemical complex analysis system have been demonstrated, and this methodology could be applied to other chemical complexes in the world for reduced emissions and energy savings. The system was developed by industry–university collaboration, and the program with users manual and tutorial can be downloaded at no cost from the LSU Mineral Processing Research Institute's website <http://www.mpri.lsu.edu>.

Introduction

Global warming is caused by accelerative accumulation of carbon dioxide and other greenhouse gases in the atmosphere. These emissions should be mitigated if the problem of global warming is to be controlled. A summary of net carbon dioxide emissions is given in Table 1 worldwide, by nations, by the United States, by U.S. industry and the chemicals, coal and refining industries. The information in this table does not include the two-way exchange of carbon dioxide between various interfaces of atmosphere, terrestrial biosphere and oceans that are given in Flannery (2000).

The U.S. accounts for 1,526 million metric tons carbon equivalent per year or about 24% of the global car-

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Table 1 CO₂ emissions and utilization (million metric tons carbon equivalent per year)

CO ₂ emissions and utilization		Reference
Total CO ₂ added to the atmosphere		
Burning fossil fuels	5,500	Flannery (2000)
Deforestation	1,600	
Total worldwide CO ₂ from consumption and flaring of fossil fuels		
United States	1,526	EIA (2002a, b)
China	792	
Russia	440	
Japan	307	
All others	3,258	
World total	6,322	
Industry	630	Song et al. (2002)
Buildings	524	
Transportation	473	
Total	1,627	
U.S. industry (manufacturing)		
Petroleum, coal products and chemicals	175	EIA (2001)
Agricultural chemical complex in the lower Mississippi		
River corridor excess high-purity CO ₂	0.183	Hertwig et al. (2002)
CO ₂ used in chemical synthesis	30	Arakawa et al. (2001)

bon dioxide emissions (EIA 2002a, b). The distribution of these emissions is among industry, buildings (heating and air conditioning) and transportation as shown in Table 1. For industrial emissions, petroleum, coal products and chemical industry are 175 of the 1,627 million metric tons carbon equivalent per year (Song et al. 2002).

Carbon dioxide emissions from these fossil fuel industries are from combustion gases and byproduct carbon dioxide, mainly from synthesis gas but also from other sources. There is an excess of 120 million tons per year of high-purity carbon dioxide from the exponential growth of ammonia production in the last 30 years (Moulijn et al. 2001) that is discharged into the atmosphere in the U.S. Ammonia production consumes hydrogen that is obtained from synthesis gas after removing carbon dioxide. About 0.61 million metric tons per year of high-purity carbon dioxide [= (44/12) × 0.183 million metric tons of carbon equivalent in Table 1] are vented from part of the plants in the chemical complex in the lower Mississippi River corridor (Hertwig et al. 2002). Also, another 19 million metric tons of relative high-purity carbon dioxide is vented from refineries and other chemical plants in the U.S. that use hydrogen from synthesis gas.

Approximately, 110 million metric tons per year of carbon dioxide are used as a raw material for the production of urea, methanol, acetic acid, polycarbonates, cyclic carbonates and specialty chemicals such as salicylic acid and carbamates (Table 1, Arakawa et al. 2001). The largest use is for urea production, which reached about 90 million metric tons per year in 1997 (Creutz and Fujita 2000). Other uses include enhanced oil recovery, solvent (supercritical carbon dioxide), refrigeration systems, carbonated beverages, fire extinguishers and inert gas-purging systems.

A potential upper limit of 650 million metric tons of carbon dioxide for use as a raw material has been estimated by Song et al. (2002). This total included traditional

processes for urea and methanol to plastics, fibers, rubber and other uses. This tonnage is comparable to carbon dioxide emissions from all U.S. fossil fuel power plants.

Research strategies for consuming excess carbon dioxide include developing new alternative processes for chemicals that have a large market and demand. For example, Hertwig et al. (2002) showed that a 100 million pound per year acetic acid plant using a new catalytic process for the direct conversion of carbon dioxide and methane to acetic acid could consume 36,700 tons per year of carbon dioxide. Also, the new process had a potential energy savings of 275 trillion BTUs per year compared to a conventional plant, and the carbon dioxide reduction from reduced steam requirements could be 12,600 tons per year. The total carbon dioxide reduction could be 49,100 tons per year compared to the conventional plant, and there could be a reduction in NO_x emissions of 3.5 tons per year based on steam and power generation by cogeneration.

Strategies proposed by Song et al. (2002) include increasing the commercial applications of products from CO₂, e.g., expanded application of urea-based polymers would increase the demand for urea, prompting an increase in CO₂ utilization. New reaction pathways could replace hazardous substances with carbon dioxide, e.g., carbon dioxide used in the production of dimethyl carbonate rather than the conventional route with phosgene as an intermediate. Other areas for increased carbon dioxide use are as a solvent for separation and as a medium for chemical reaction based on its physical and chemical properties. Carbon dioxide use could be expanded in enhanced recovery of crude oil and coal bed methane. Here, low-purity carbon dioxide is acceptable, and processing costs for separation and purification would be decreased.

The costs for sequestering carbon dioxide in geological formations, oceans and natural systems have been summarized by Kim and Edmonds (2000). They esti-

mated the current cost to range from \$120 to \$340 per metric ton of carbon equivalent, which may drop to \$50 per ton of carbon equivalent by 2015. The annual production of U.S. synthetic plastics was about 36.7 million metric tons in 1999. These plastics eventually will be sequestered in a landfill at the end of their useful life. By converting carbon dioxide to plastics, the chemical industry can make a profit and at the same time contribute to sequestration of carbon dioxide. This approach could be a more effective way of storing carbon dioxide rather than directly sequestering it.

A sulfur dioxide (SO₂) emission-trading program that is part of the 1990 Clean Air Act Amendments has been very successful. The Kyoto Protocol would aggregate greenhouse gases (GHG) emissions not to exceed an assigned amount and that would lead to carbon emissions trading among countries. Emission trading is a mechanism for lowering the cost of meeting environmental performance goals in three ways. The first is that trading allows companies with low-cost emission reduction opportunities to reduce their emissions below the limits prescribed by the cap, and they can sell their surplus reduction to companies facing limits whose reduction costs are higher. The second is creating financial incentives for companies that lower their emissions with a market for surplus reductions; emissions trading spurs the development of new emissions control technologies and techniques. The third is that creative new approaches to emissions prevention are encouraged because emission trading gives businesses flexibility to meet their emission limits. The critical advantage of emissions trading is that it allows society to get more pollution prevention for every dollar spent on emissions reductions. Voluntary emission trading of greenhouse gases is underway in the U.S. and Europe, and some companies are banking carbon credits by purchasing forest. Greenhouse gas value is between \$5 per ton and \$35 per ton of carbon in the USA, Canada and Costa Rica. Additional details are given by Xu (2004).

The objectives of this research were to identify and design new industrial processes that use carbon dioxide as a raw material and show how these processes could be integrated into existing chemical production complexes. The chemical production complex in the lower Mississippi River corridor was used to demonstrate the integration of these new plants into an existing infrastructure. New processes were evaluated based on selection criteria, and simulations of these processes were performed using HYSYS. Then the optimal configuration of new and existing plants was determined by optimizing the triple bottom line based on the net of product revenue and manufacturing cost, and environmental and sustainable costs along with satisfying process constraints using the chemical complex analysis system.

Chemical complex optimization is a powerful methodology for plant and design engineers to convert their company's goals and capital to viable projects that meet economic, environmental and sustainable requirements. The optimal configuration of plants in a chemical pro-

duction complex is obtained by solving a mixed integer nonlinear programming (MINLP) problem. The chemical production complex of existing plants in the lower Mississippi River corridor was a base case for evaluating the additions of new plants that used carbon dioxide as a raw material. These results are applicable to other chemical production complexes in the world including the ones in the Houston area (largest in the world), Antwerp port area (Belgium), BASF in Ludwigshafen (Germany), Petrochemical district of Camacari-Bahia (Brazil), the Singapore petrochemical complex on Jurong Island (Singapore), and Equate (Kuwait), among others.

New processes using carbon dioxide as a raw material

Carbon dioxide reactions

Carbon dioxide can be used as a reactant in heterogeneous or homogeneous catalytic and non-catalytic processes. Also, it can be used in photochemical, photocatalytic reduction, bio-chemical, and electro-catalytic conversions. It can be used as the whole molecule in reactions, and it can be used as a carbon source or as an oxygen source (Creutz and Fujita 2000). There have been five international conferences (Song et al. 2002; Steinberg and Halmann 1999; Inui et al. 1998; Sullivan 1993; Inoue and Yamazaki 1982) and numerous articles in the past 20 years on carbon dioxide reactions that consider using it as a raw material. It is an inexpensive and nontoxic starting material (Creutz and Fujita 2000) and represents a possible potential source for the manufacture of chemicals (Keene 1993).

The carbon dioxide molecule has a linear structure. It is a thermodynamically stable molecule with bond strength measured at $D = 532$ kJ/mol (Keene 1993). The heat of formation at 25 C (ΔH) is -393.5 kJ/mol, and Gibbs free energy of formation at 25 C (ΔG) is -394.3 kJ/mol. These values were used to evaluate the standard heat of reaction and Gibbs free energy change for CO₂ reactions (Song et al. 2002). Some reactivity is anticipated for carbon dioxide despite its linear symmetry and overall nonpolar nature because of the presence of π -electron density of the double bonds and the lone pairs of electrons on the oxygen atoms, or the electrophilic carbon atom (Keene 1993). Reactions of carbon dioxide are dominated by nucleophilic attacks at the carbon atom, which result in the bending of the O-C-O angle to about 120° (Creutz and Fujita 2000).

Catalytic reactions of CO₂ that produce industrially important chemicals are listed in Table 2. Reactions were categorized as hydrogenation reactions producing alcohols; hydrocarbon synthesis reactions producing paraffins and olefins; amine syntheses producing methyl and higher order amines; and hydrolysis reactions producing alcohols and organic acids. Also, carbon dioxide can serve as an oxygen source in the ethyl benzene-to-styrene reaction, and it can be used in dehydrogenation and reforming reactions. A comprehensive discussion of

Table 2 Summary of catalytic reactions of carbon dioxide (Hertwig et al. 2002)

Hydrogenation	
$\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	Methanol
$2\text{CO}_2 + 6\text{H}_2 \rightarrow \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O}$	Ethanol
$\text{CO}_2 + \text{H}_2 \rightarrow \text{CH}_3\text{OCH}_3$	Dimethyl ether
Hydrocarbon synthesis	
$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	Methane and higher HC
$2\text{CO}_2 + 6\text{H}_2 \rightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O}$	Ethylene and higher olefins
Carboxylic acid synthesis	
$\text{CO}_2 + \text{H}_2 \rightarrow \text{HCOOH}$	Formic acid
$\text{CO}_2 + \text{CH}_4 \rightarrow \text{CH}_3\text{COOH}$	Acetic acid
Graphite synthesis	
$\text{CO}_2 + \text{H}_2 \rightarrow \text{C} + \text{H}_2\text{O}$	Graphite
$\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	
$\text{CH}_4 \rightarrow \text{C} + \text{H}_2$	
Amine synthesis	
$\text{CO}_2 + 3\text{H}_2 + \text{NH}_3 \rightarrow \text{CH}_3\text{NH}_2 + 2\text{H}_2\text{O}$	Methylamine and higher amines
Hydrolysis and photocatalytic reduction	
$\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{O}_2$	Methanol
$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{HCOOH} + 1/2 \text{O}_2$	Formic acid
$\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_4 + 2\text{O}_2$	Methane
Other reactions	
$\text{C}_6\text{H}_5\text{C}_2\text{H}_5 + \text{CO}_2 \rightarrow \text{C}_6\text{H}_5\text{C}_2\text{H}_3 + \text{CO} + \text{H}_2\text{O}$	Styrene
$\text{CO}_2 + \text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_6 + \text{H}_2 + \text{CO}$	Propylene
$\text{CO}_2 + \text{CH}_4 \rightarrow 2\text{CO} + \text{H}_2$	Reforming

carbon dioxide reactions in organic synthesis is given by Haruki (1982).

The results of a detailed review of the literature for the reactions of carbon dioxide are given by Indala (2004). Eighty-six published articles of laboratory and pilot plant experiments were found and reviewed that describe new methods and catalysts to use carbon dioxide for producing commercially important products. These reactions were categorized as shown in Table 2. For each of these articles Indala (2004) reported the operating conditions (temperature, pressure and space velocity), catalyst used, reactant conversion and selectivity, and products from these experimental studies. Also included were evaluations of heat of reaction and the free energy change for the reactions. These results were used for the design of new processes that use carbon dioxide as a raw material.

New process selection

A methodology for selecting new energy-efficient and environmentally acceptable processes has been developed. The selection criteria included operating conditions, energy requirement for reactions, ΔH , and thermodynamic feasibility and equilibrium conversion of reactions based on Gibbs free energy change, ΔG . Catalyst conversion and selectivity, cost and life (time on stream to deactivation), and methods to regenerate catalysts were considered. Also included were raw material availability, product demand and market penetration. In addition, raw materials, energy, environmental, and sustainable costs were evaluated.

If a new process appeared to have advantages over an existing commercial process, then it was selected for HYSYS simulation. For example, if a new process operated at a lower temperature and pressure than the

conventional process with a comparable space velocity and catalyst, there would be the potential to reduce both operating costs and energy requirements.

Pacific Northwest National Laboratory (PNNL) estimated potential energy savings for 26 commercial chemicals through improved catalysts (Pellegrino 2000). The list of these commercial chemicals with estimated energy savings is shown in Table 3. Comparing this list in Table 3 to the reactions in Table 2, propylene, methanol, acetic acid and styrene are on both with a potential energy savings of 98, 37, 2 and 20 trillion BTUs per year, respectively.

Another criterion was based on energy requirements and thermodynamic feasibility of reactions based on the heat of reaction, ΔH , and the standard Gibbs free energy change, ΔG , of the reactions. Positive values of ΔH indicate that a reaction is endothermic, and a process operating with an endothermic reaction requires energy be supplied for the reaction with a corresponding energy cost. In processes with exothermic reactions, energy is released, and this energy can be recovered for process heating needs. Such a process will have the potential to reduce the total energy costs in a chemical complex.

According to Dodge (1944), reactions are said to be less feasible as ΔG increases in a positive direction, but there is no definite value that can be chosen as clearly indicating that a reaction is not feasible from the standpoint of industrial operations. For example, the methanol synthesis reaction ΔG is +11,000 cal/g-mol at 600 K, and this reaction is certainly feasible. Dodge (1944) provides the following guidelines for the purpose of ascertaining quickly and only approximately if any given reaction is promising at a given temperature.

If ΔG of a reaction is less than 0, then the reaction is said to be promising. If it is positive and is less than 10,000 cal/g-mol (42 kJ/g-mol), then the reaction is of

Table 3 Potential energy savings through improved catalysts in trillion BTUs (Pellegrino 2000)

Chemical	Rank	Total energy savings
Ammonia	1	294
Propylene	2	98
<i>p</i> -Xylene	3	94
Butadiene	4	81
Vinyl chloride	5	44
Methanol	6	37
Ethylene oxide	7	29
Acrylonitrile	8	24
Adipic acid	9	20
Styrene	10	20
Vinyl acetate	11	16
Propylene oxide	12	16
Phenol	13	12
Ethylene dichloride	14	11
Acetone	15	8
Terephthalic acid	16	8
Formaldehyde	17	6
Ethylbenzene	18	4
Cumene	19	3
Acetic acid	20	2
Nitric acid	21	1
MTBE	22	1
Caprolactam	23	1
Ethylene glycol	24	1
Sulfuric acid	25	1
Isobutylene	26	0.3

doubtful promise but warrants further study. If ΔG is further positive than 10,000 cal/g-mol, then the reaction is unfavorable and would be feasible only under unusual circumstances (Dodge 1944). As ΔG increases, the equilibrium distribution of reaction products becomes less favorable. The above guidelines were used in estimating the thermodynamic feasibility of a reaction when considering a new process.

There are ways to increase the conversion for reactions having a positive ΔG . One standard procedure is to remove the products in an intermediate step. This

method is used in the double absorption contact process for sulfuric acid where sulfur trioxide is removed after the gas passes through two packed bed reactors before entering the last two reactors.

Another criterion used for selection of new processes was the cost of raw materials and sales of products. Internally produced raw materials are usually less expensive than those purchased on the open market. For example, in certain CO₂ hydrogenation reactions, the conversion can be increased if the mole ratio of H₂/CO₂ ratio is high (3–4), and there is a trade-off with cost and conversion since hydrogen is an expensive raw material. If hydrogen is formed as a by-product in another new process, it could provide a source for less expensive hydrogen. A new process for propylene manufacture from propane produces hydrogen as a by-product, and it can be used for this purpose as described in the next section.

The criteria described above were applied to the results in 86 published articles of laboratory and pilot plant experiments that described new methods and catalysts using carbon dioxide to produce commercially important products. From these, 20 of the most promising were selected for process designs using HYSYS, and these designs gave the information required for one to evaluate a value added economic analysis for each process. These processes included production of methanol, ethanol, dimethyl ether, propylene, formic acid, acetic acid, styrene, methylamines, graphite, and synthesis gas, and they are listed in Table 4. Key selection criteria included lower operating temperature and pressure, effective catalyst, significant energy savings, product demand and environmental acceptability.

HYSYS.Plant.2.2 (HYSYS) is a flow-sheeting program from Hyprotech that can be used to create rigorous steady state and dynamic models for plant design. HYSYS was used for simulating new processes with production capacities that were comparable to existing plants in the lower Mississippi River corridor. Conver-

Table 4 New processes selected for process design using HYSYS

Chemical	Synthesis route	Reference
Methanol	CO ₂ hydrogenation	Nerlov and Chorkendorff (1999) Toyir et al. (1998) Ushikoshi et al. (1998) Jun et al. (1998) Bonivardi et al. (1998)
Ethanol	CO ₂ hydrogenation	Inui (2002) Higuchi et al. (1998)
Dimethyl ether	CO ₂ hydrogenation	Jun et al. (2002)
Formic acid	CO ₂ hydrogenation	Dinjus (1998)
Acetic acid	From methane and CO ₂	Taniguchi et al. (1998)
Styrene	Ethylbenzene dehydrogenation	Sakurai et al. (2000) Mimura et al. (1998)
Methylamines	From CO ₂ , H ₂ , and NH ₃	Arakawa (1998)
Graphite	Reduction of CO ₂	Nishiguchi et al. (1998)
Hydrogen/synthesis gas	Methane reforming	Song et al. (2002) Shamsi (2002) Wei et al. (2002) Tomishige et al. (1998)
Propylene	Propane dehydrogenation	Takahara et al. (1998) C & EN (2003)

sion reactors were used to evaluate products formed from reactants. Heat exchanger duties gave estimates for steam and cooling water requirements. Distillation columns were used for separations of products from reactants that were recycled.

A value-added economic analysis was developed from each of the HYSYS simulation, which required specifying product price and sales, raw material cost and use, and utility costs. The other operating costs that go into the total product cost, and a return on investment for the plant cost were not included, and these costs would reduce the profit predicted from a value-added economic model. If a process were not profitable based on the value-added economics, it would not be profitable with the other costs included. The procedure for evaluating value-added economic cost analysis is given by the equation:

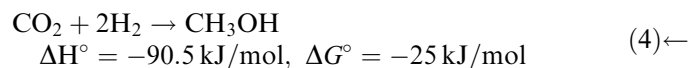
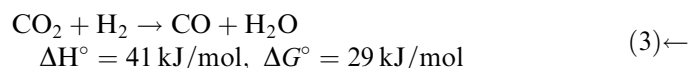
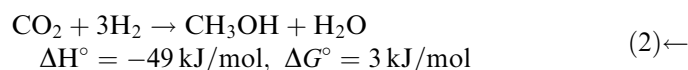
$$\text{Profit} = \sum \text{product sales} - \sum \text{raw material costs} - \sum \text{energy costs} \quad (1)$$

Product sales prices and raw material costs were obtained from the Chemical Market Reporter (2000, 2002a, b), Turton et al. (1998), C & EN (2003) and Camford Chemical Prices (2000). Plant production capacities were based on plants in the lower Mississippi River corridor or an average production rate in the U.S. The raw material cost for high-purity (99%) CO₂ was \$3.00 per ton, the cost of delivering it from a pipeline (T. A. Hertwig, Private Communication). The CO₂ feed used in all the processes was at 100 psi and 30 C, pipeline pressure and temperature. The cost of CO (\$31 per ton) was not available from the Chemical Market Reporter, and it was based on its heating value as a fuel. The cost of pipeline hydrogen (\$796 per ton) was based on the cost of methane as given by G.P. Kuehler (personal communication). High-pressure (HP) steam was used for process heating (47 bar, 260 C, specific heat of 1.067 kcal/kg C) with a heat of vaporization of 1661.5 kJ/kg (Smith et al. 1996) and cost of \$8.65 per ton (Turton et al. 1998). Cooling water was used in heat exchangers and condensers where energy was removed from process streams, and it was heated from 30 C to 50 C. Excess scaling occurs above this temperature (Turton et al. 1998). The cost of cooling water was \$6.7 per 1,000 m³ (Turton et al. 1998). The electrical energy used was not included, since this cost required itemizing pumps, compressors and auxiliaries.

Evaluations are given in Tables 5 and 6 for two processes: carbon dioxide hydrogenation to methanol (Ushikoshi et al. 1998) and acetic acid synthesis from carbon dioxide and methane (Taniguchi et al. 1998). These evaluations illustrate the procedure used, and all of the evaluations are given in Indala (2004).

Methanol from CO₂ hydrogenation over Cu/ZnO/ZrO₂/Al₂O₃/Ga₂O₃

The experimental study of Ushikoshi (1998) was used to develop a process for the production of methanol by CO₂ hydrogenation using HYSYS. A multicomponent catalyst (Cu/ZnO/ZrO₂/Al₂O₃/Ga₂O₃) was used in this new process. The CO₂ conversion per pass was 17% (Ushikoshi 1998), and complete conversion of CO₂ was achieved by recycling the unreacted feed. The reactions involved in the reactor are:



The methanol production rate of this simulated process was 479,800 metric tons per year (54,730 kg/h). This was based on Ashland Chemical Inc., a methanol plant located in Plaquemine, LA, USA, and the production rate of this plant is 160 million gallons per year (480,846 metric tons/year) (Louisiana Chemical & Petroleum Products List 1998). The purity of methanol produced was 99%, and carbon monoxide was obtained as by-product.

The steam and cooling water requirements for the process were determined from the HYSYS process flow diagram. The energy required for high pressure (HP) steam was 1,152×10⁶ kJ/h, and this corresponded to 693×10³ kg/h of steam as shown in Table 5. The energy removed by cooling water was 138×10⁷ kJ/h, and this corresponded to 1,651×10⁴ kg/h of cooling water. Also, the amount of CO₂ that could be consumed by this process was estimated to be 670,150 metric tons per

Table 5 Economic results for the HYSYS simulated methanol production process by Ushikoshi (1998)

Product/raw material	Flow rate from HYSYS simulation (kg/h)	Cost/selling price (\$/kg)	Reference
Carbon dioxide	76,450	0.003	T. A. Hertwig, private communication
Hydrogen	10,420	0.796	Indala 2004
Methanol	54,730	0.300	Chemical Market Reporter (2003)
Carbon monoxide	585	0.031	Indala 2004
HP steam	693×10 ³	0.00865	Turton et al. (1998)
Cooling water	1,651×10 ⁴	6.7×10 ⁻⁶	Turton et al. (1998)
Value-added profit	\$1,810/h	3.3 cents/kg-methanol	

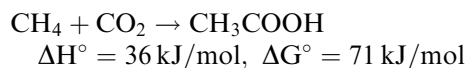
Table 6 Economic results for the HYSYS simulated process for the production of acetic acid base on the data of Taniguchi et al. (1998)

Product/raw material	Flow rate from HYSYS simulation (kg/h)	Cost/selling price (\$/kg)	Reference
Carbon dioxide	685	0.003	T. A. Hertwig, personal communication
Methane	249	0.172	G.P. Kuehler, personal communication
Acetic acid	933	1.034	Chemical Market Reporter (2002a, b)
High pressure steam	766	0.00865	Turton et al. (1998)
Cooling water	13,730	6.7×10^{-6}	Turton et al. (1998)
Value-added profit	\$913/h	97.9 cents/kg-acetic acid	

year. As shown in Table 5, the value-added economic model gave a profit of 3.3 cents per kg methanol.

Acetic acid from carbon dioxide and methane

The experimental study of Taniguchi et al. (1998), was used to develop a process for the production of acetic acid using HYSYS. Acetic acid was produced according to the reaction given by Eq. 5. The catalyst was VO(acac)₂ (acac: acetylacetonate), and the acetic acid yield based on CH₄ was 97%. An 80% excess of carbon dioxide was required in the reactor, and the carbon dioxide was recycled achieving a complete conversion of reactants. Acetic acid with 100% purity was produced.



The production rate of this simulated plant was selected to be 8,175 metric tons/year (933 kg/h). This rate was based on Union Carbide Corporation's acetic acid plant located in Hahnville, LA, USA, and the production rate of this plant is 18 million lb/year (8,165 metric tons/year) (Louisiana Chemical & Petroleum Products List 1998).

Based on the HYSYS flow sheet, the energy required HP steam was $1,273 \times 10^3$ kJ/h and this corresponds to 766 kg/h of steam as shown in Table 6. The energy removed by the cooling water was $1,148 \times 10^3$ kJ/h, and

this corresponds to 3,730 kg/h of cooling water. The amount of CO₂ that could be consumed by this new process was 6,005 metric tons of CO₂ per year. The value-added economic model gave a profit of 97.9 cents per kg acetic acid as shown in Table 6.

Summary

The value-added profits for the 20 new processes are summarized in Table 7 and 8. Based on this value-added economic evaluation, 14 new processes were selected to be included in the chemical complex, and these are listed in Table 7. These processes include production of methanol, ethanol, dimethyl ether, propylene, formic acid, acetic acid, styrene, methylamines, graphite and synthesis gas. The processes that were not included in the chemical complex are listed in Table 8. Based on the value-added economic analysis, these processes were not economically competitive with other simulated plants for the same product and existing commercial processes.

Comparison with other new carbon dioxide pilot plants

Two pilot plants that use carbon dioxide as a raw material have been reported. One is operated by Nano-Tech Research Center of the Korea Institute of Science and Technology (KIST). They have been operating a 100 kg/day methanol pilot plant since April 2002 using CO₂ as a raw material, (Ondrey 2003), and a demon-

Table 7 New processes included in the chemical production complex

Product	Synthesis route	Value-added profit (cents/kg)	Reference
Methanol	CO ₂ hydrogenation	2.8	Nerlov and Chorkendorff (1999)
Methanol	CO ₂ hydrogenation	3.3	Ushikoshi (1998)
Methanol	CO ₂ hydrogenation	7.6	Jun et al. (1998)
Methanol	CO ₂ hydrogenation	5.9	Bonivardi et al. (1998)
Ethanol	CO ₂ hydrogenation	33.1	Higuchi et al. (1998)
Dimethyl ether	CO ₂ hydrogenation	69.6	Jun et al. (2002)
Formic acid	CO ₂ hydrogenation	64.9	Dinjus (1998)
Acetic acid	From CH ₄ and CO ₂	97.9	Taniguchi et al. (1998)
Styrene	Ethylbenzene dehydrogenation	10.9	Mimura et al. (1998)
Methylamines	From CO ₂ , H ₂ , and NH ₃	124	Arakawa (1998)
Graphite	Reduction of CO ₂	65.6	Nishiguchi et al. (1998)
Hydrogen/synthesis gas	Methane reforming	17.2	Shamsi (2002)
Propylene	Propane dehydrogenation	4.3	Takahara et al. (1998)
Propylene	Propane dehydrogenation with CO ₂	2.5	C & EN (2003)

Table 8 New processes not included in the chemical production complex

Product	Synthesis route	Value-added profit (cents/kg)	Reference
Methanol	CO ₂ hydrogenation	-7.6	Toyir et al. (1998)
Ethanol	CO ₂ hydrogenation	31.6	Inui (2002)
Styrene	Ethylbenzene dehydrogenation	4.5	Sakurai et al. (2000)
Hydrogen/synthesis gas	Methane reforming	17.2	Song et al. (2002)
		17.1	Wei et al. (2002)
		17.1	Tomishige et al. (1998)

stration plant is planned. In this process, carbon dioxide and hydrogen are reacted to produce CO and H₂O over a ZnAl₂O₄ catalyst. The reaction occurs at atmospheric pressure and 600–700 C. Water is removed from the mixture in a dryer. In a second reactor, carbon monoxide reacts with unreacted hydrogen over a CuO/ZnO/ZrO₂/Al₂O₃ catalyst to produce methanol. This reaction occurs at 250–300 C and 50–80 atm pressure.

The other is a 50-kg per day pilot plant described by Ushikoshi 1998 that is operated by the Japanese National Institute for Resources and Environment. In this unit a (Cu/ZnO/ZrO₂/Al₂O₃/Ga₂O₃) catalyst was used in a methanol reactor that operated at 350 C and 5 MPa (50 atm). This pilot plant was used for the HYSYS design described previously that used reactions 7, 8 and 9 for the production of methanol.

Production cost of methanol for the KIST pilot plant is \$300 per metric ton, and full-scale plants based on this technology were estimated to have a production cost of \$100 per metric ton. The value-added economic model for the HYSYS simulated methanol plants gave a profit of 2.8–7.6 cents per kg (\$28–\$76 per metric ton) of methanol.

In summary, the HYSYS-simulated methanol plants were comparable to two actual pilot plants operated by Nano-Tech Research Center of the KIST and the Japanese National Institute for Resources and Environment. This comparison shows the feasibility of new processes using carbon dioxide being commercialized in future.

Incorporating carbon dioxide processes in the chemical complex

The results of the HYSYS simulations gave 14 new processes that can be integrated into the chemical production complex in lower Mississippi River corridor. There are about 150 chemical plants in this complex that consume 1.0 quad (10¹⁵ BTUs per year) of energy and generate about 215 million pounds per year of pollutants (Peterson 1999). A carbon dioxide pipeline connects several plants, and the cost of excess high-purity carbon dioxide is essentially the pumping cost of about \$3 per ton, since it is being vented to the atmosphere now.

With the assistance of industrial collaborators, a base case of existing plants was developed that includes the sources and consumers of carbon dioxide in the chemical production complex in the lower Mississippi River cor-

ridor. This chemical production complex (base case) is shown in Fig. 1. There are 13 production units plus associated utilities for power, steam and cooling water and facilities for waste treatment. A production unit contains more than one plant. For example, the sulfuric acid production unit contains five plants owned by two companies (Hertwig et al. 2002). Here, ammonia plants produce 0.75 million tons/year of carbon dioxide, and methanol, urea, and acetic acid plants consume 0.14 million tons of carbon dioxide. This leaves a surplus of 0.61 million tons/year of high-purity carbon dioxide. This high-purity carbon dioxide is being vented to the atmosphere now. It is available through pipelines to be used as a raw material in new plants.

As shown in Fig. 1, the raw materials used in the chemical complex include: natural gas, sulfur, ethylene, benzene, phosphate rock, air and water. The products include mono- and di-ammonium phosphates (MAP and DAP), granular triple super phosphate (GTSP), urea, urea ammonium nitrate solution (UAN), ammonium sulfate, phosphoric acid, acetic acid, styrene and methanol. Intermediates formed include nitric acid, sulfuric acid, ammonia, methanol, carbon dioxide, ethyl benzene and phosphoric acid. Sulfuric acid is used to produce phosphoric acid that is used to produce mono- and di-ammonium phosphates. Ammonia from the ammonia plant is used to produce nitric acid and ammonium nitrate, and carbon dioxide from this plant is used to produce urea, methanol and acetic acid. The steps for other products are shown on the diagram, as is the venting of excess high-purity carbon dioxide from the ammonia plant (0.61 million metric tons per year).

The chemical complex analysis system is used to determine the optimum configuration of plants in a chemical complex based on the AIChE total cost assessment (TCA) report for economic, energy, environmental and sustainable costs (Constable et al. 1999). This system uses a flowsheeting program with a graphical user interface where material and energy balances, rate equations and equilibrium relations are entered for each plant along with production capacities, product demand and raw material availability. The system writes and runs a GAMS program to solve the mixed integer optimization problem and presents the results to the user in tables and on the process flow diagram. It also incorporates the EPA waste reduction algorithm (WAR) algorithm. A detailed description of the system is given by Hertwig et al. (2002).

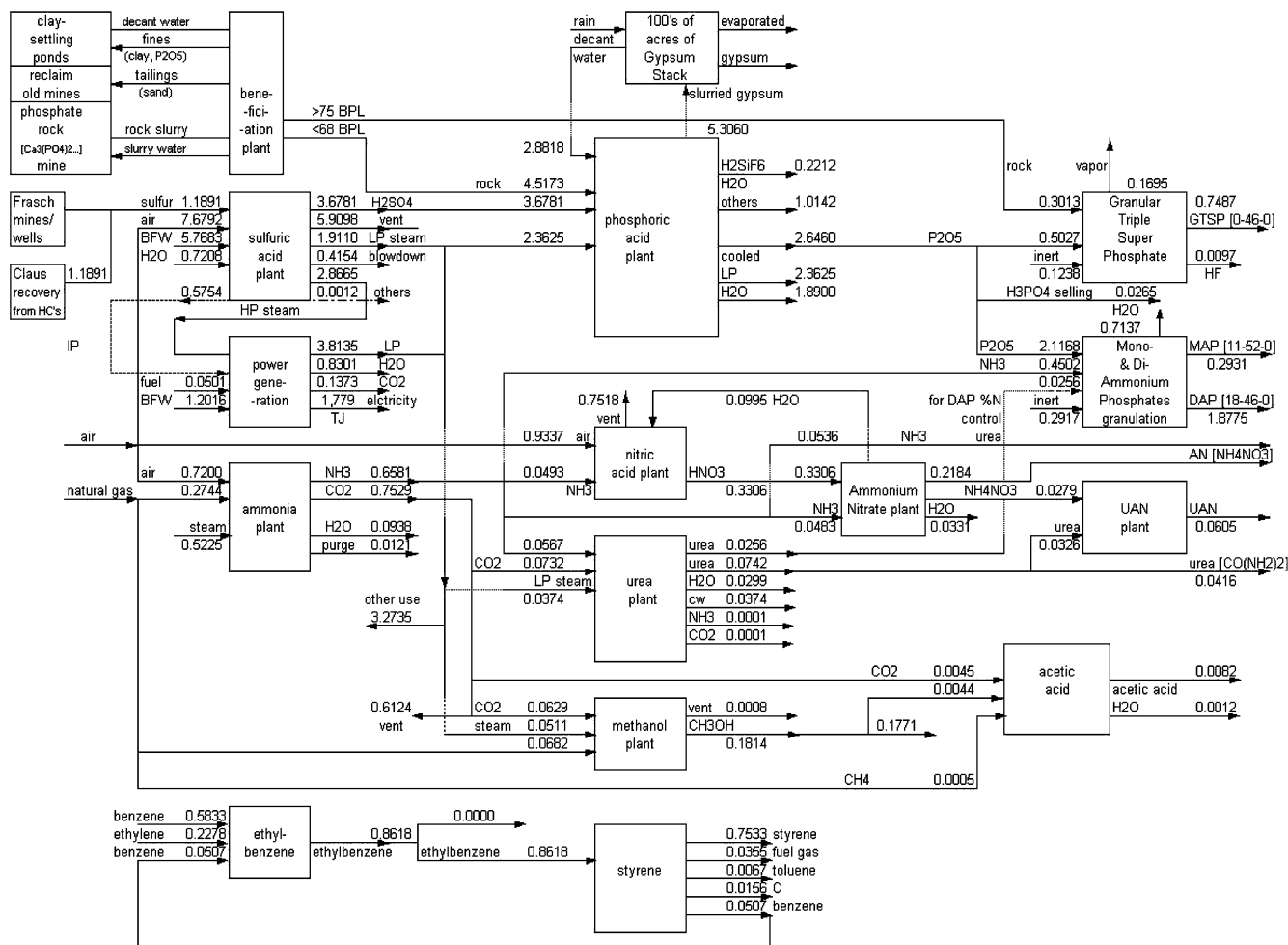


Fig. 1 Base case of existing plants in the chemical production complex in the lower Mississippi River corridor. Flow rates in million metric tons per year

For this base case, there are 270 equality constraints that describe material and energy balances, rate equations and equilibrium relations for these plants. Also, there are 28 inequality constraint equations that describe the product demand, raw material availability, and range of capacities of individual plants in the chemical complex (Hertwig et al. 2002). The model of the complex is available in the chemical complex analysis system program available from the LSU Mineral Processing Research Institute's website, <http://www.mpri.lsu.edu> (Xu et al. 2004).

The chemical production complex shown in Fig. 1 was expanded into a superstructure by integrating the 14 new processes from Table 7 that were selected based on the evaluations of HYSYS simulations. The diagram of plants in the superstructure is given by Indala (2004), and a convenient way to show the plants in the base case and plants added to form the superstructure is given in Table 9. These processes include four processes for methanol production, two processes for propylene, and one process each for ethanol, dimethyl ether, formic acid, acetic acid, styrene, methylamines, graphite and

synthesis gas. This expanded complex gives alternative ways to produce intermediates that reduce wastes and energy and consume greenhouse gases.

Four other new processes developed by Xu et al. (2003) that do not use CO₂ as a raw material were included in the superstructure. Two additional plants were added to produce phosphoric acid. One is the electric furnace process, which has high-energy costs but produces calcium oxide. In the other process, calcium phosphate ore reacts with hydrochloric acid to produce phosphoric acid. Also, there are two plants that use gypsum wastes to recover sulfur and sulfur dioxide. One reduces gypsum waste to sulfur dioxide that is recycled to the sulfuric acid plant. The other reduces gypsum waste to sulfur and sulfur dioxide that is recycled to sulfuric acid plant. A total of 18 new processes were included in the superstructure with the base case plants as shown in Table 9.

In summary, the superstructure includes three options for producing phosphoric acid, five options for producing methanol, and two options each for producing acetic acid, styrene and propylene. Also, it includes two options for recovering sulfur and sulfur dioxide. It includes plants producing sulfuric acid, nitric acid, urea, urea ammonium nitrate solution (UAN), granular triple

Table 9 Processes in chemical production complex base case and superstructure

Plants in the base case	Plants added to form the superstructure
Ammonia	Methanol (Bonivardi et al. 1998)
Nitric acid	Methanol (Jun et al. 1998)
Ammonium nitrate	Methanol (Ushikoshi et al. 1998)
Urea	Methanol (Nerlov and Chorkendorff 1999)
UAN	Ethanol
Methanol	Dimethyl ether
Granular triple super phosphate (GTSP)	Formic acid
MAP and DAP	Acetic acid (new process)
Contact process for sulfuric acid	Styrene (new process)
Wet process for phosphoric acid	Methylamines (MMA and DMA)
Acetic acid	Graphite
Ethyl benzene	Synthesis gas
Styrene	Propylene from CO ₂
Power generation	Propylene from propane dehydrogenation
	Electric furnace process for phosphoric acid
	HCl process for phosphoric acid
	SO ₂ recovery from gypsum waste
	S and SO ₂ recovery from gypsum waste

super phosphate (GTSP), mono- and di-ammonium phosphates (MAP and DAP), ethylbenzene, graphite, synthesis gas, dimethyl ether (DME), formic acid, ethanol, and methylamines [monomethylamine (MMA) and dimethylamine (DMA)].

Table 10 Raw material costs, product prices and sustainable costs and credits (Constable et al. 1999; Chemical Market Reporter 2000, 2002a, b, 2003; Camford Chemical Prices 2000; C&EN 2003)

Raw materials	Cost (\$/mt)	Standard deviation (\$/mt)	Sustainable cost and credits	Cost /credit (\$/mt)	Products	Price (\$/mt)	Standard deviation (\$/mt)
Natural gas	235	69.4	Credit for CO ₂ consumption	6.50	Ammonia	224	17.7
Phosphate rock			Debit for CO ₂ production	3.25	Methanol	271	43.2
Wet process	27	–	Debit for NO _x production	1,030	Acetic acid	1,030	36.6
Electric furnace	34	–	Debit for SO ₂ production	192	GTSP	132	–
Haifa process	34	–	Credit for gypsum consumption	5.0	MAP	166	4.20
GTSP process	32	–	Debit for gypsum production	2.5	DAP	179	7.89
HCl	95	11.1			NH ₄ NO ₃	146	6.66
Sulfur					Urea	179	17.4
Frasch	53	9.50			UAN	120	–
Claus	21	3.55			Phosphoric acid	496	–
Coke	124	–			Hydrogen	1,030	252
electric furnace							
Propane	180	–			Ethylbenzene	556	75.9
Benzene	303	60.3			Styrene	824	94.7
Ethylene	565	95.4			Propylene	519	66.0
Reducing gas	75	–			Formic acid	690	–
Wood gas	88	–			MMA	1,610	–
					DMA	1,610	–
					DME	946	–
					Ethanol	933	23.1
					Toluene	384	47.7
					Graphite	904	82.0
					Fuel gas	784	–
					CO	45	13.3

To determine the optimum configuration of plants in the chemical complex, a value-added economic model given by the profit in Eq. 1 was expanded to account for environmental and sustainable costs. Environmental costs are costs required to comply with Federal and state environmental regulations including permits, monitoring emissions, fines, etc., as described in the AIChE/TCA report (Constable et al. 1999). Sustainable costs are costs to society due to damage to the environment, caused by emissions discharged within permitted regulations. This extended value-added economic model is referred to as the “triple bottom line” and is the difference between sales and sustainable credits and economic costs (raw materials and utilities), environmental costs and sustainable costs as given by Eq. 6. The sales prices for products and the costs of raw materials are given in Table 10 along with sustainable costs and credits.

$$\begin{aligned} \text{Triple bottom line} = & \sum \text{product sales} - \sum \text{raw material} \\ & \text{costs} - \sum \text{energy costs} \\ & - \sum \text{environmental costs} \\ & + \sum \text{sustainable (credits - costs)} \quad (6) \leftarrow \end{aligned}$$

$$\begin{aligned} \text{Triple bottom line} = & \text{profit} - \sum \text{environmental costs} \\ & + \sum \text{sustainable (credits - costs)} \leftarrow \end{aligned}$$

Environmental costs are costs required to comply with Federal and state environmental regulations including permits, monitoring emissions, fines, etc., as described in the AIChE/TCA report (Constable et al.

1999). These costs were estimated to be 67% of the raw material costs based on the data provided by Amoco, Dupont and Novartis in the AIChE/TCA report (Constable et al. 1999). This report lists environmental costs and raw material costs as approximately 20% and 30% of the total manufacturing costs, respectively.

Sustainable costs were estimated from results given for power generation in the AIChE/TCA report where CO₂ emissions had a sustainable cost of \$3.25 per ton of CO₂. As shown in Table 9, a cost of \$3.25 was charged as a cost to plants that emit CO₂, and a credit of twice this cost (\$6.50) was given to plants that utilized CO₂. In this report SO₂ and NO_x emissions had sustainable costs of \$192 per ton of SO₂ and \$1,030 per ton of NO_x. In addition, for gypsum production and use, an arbitrary but conservative sustainable cost of \$2.5 per ton for gypsum production was used, and a credit of \$5.0 per ton for gypsum consumption was used.

For optimization, upper and lower bounds of the production capacities of plants in the complex are required. The upper bounds for the new processes were from the HYSYS simulations that were based on actual plants. For convenience, the lower bound for the production rate was selected as half the value of upper bound. If a process is selected, it has to operate at least at the lower bound of its production rate. The upper bounds and lower bounds of the production rates associated with the plants in the chemical complex are shown in a subsequent table, Table 15.

For mixed integer optimization, binary variables are associated with the production capacities of each plant. If the binary variable for a process is one, then the plant operates at least at its lower bound on the production rate. If the binary variable of a process is zero, then the production rate of that process is zero, and the plant is not in the optimal structure. Relations among the binary variables and the logic constraints used in the System are given in Table 11, and the binary variables associated with the plants are given in Table a:

Acetic acid (Y ₁₁)	Acetic acid, new process (Y ₁₂)
SO ₂ recovery from gypsum (Y ₁₃)	S and SO ₂ recovery from gypsum (Y ₁₄)
Phosphoric acid, electric furnace (Y ₁)	Phosphoric acid, Haifa process (Y ₂)
Phosphoric acid, wet process (Y ₃)	Methanol (Y ₁₆)
Methanol, Jun et al. (1998) (Y ₃₁)	Methanol, Bonivardi et al. (1998) (Y ₃₂)
Methanol, Nerlov and Chorkendorff (1999)	(Y ₃₃) Methanol, Ushikoshi et al. (1998) (Y ₃₄)
Styrene-new process (Y ₃₅)	Styrene (Y ₄₀)
Ethyl benzene (Y ₄₁)	Formic acid (Y ₂₉)
Methylamines (Y ₃₀)	Ethanol (Y ₃₇)
Dimethyl ether (Y ₃₈)	Propylene from CO ₂ (Y ₂₃)
Propylene from propane dehydrogenation (Y ₂₄)	
Synthesis gas (Y ₂₇)	Graphite (Y ₃₉)

Referring to Table 11, the conventional processes and the corresponding new processes were compared to each other for acetic acid, S and SO₂ recovery, methanol and styrene; and the best processes were selected. Also, hydrogen must be available for plants that require hydrogen for them to be included in the complex.

The superstructure has 735 continuous variables, 23 integer variables, and 601 equality constraint equations for material and energy balances. Also, there are 77 inequality constraints for availability of raw materials, demand for products, capacities of the plants in the complex and logical relations. The degrees of freedom are 134, and the optimal solution obtained with the chemical complex analysis system is discussed below.

Optimal configuration of plants in the complex

The optimum configuration of plants was obtained from the superstructure by maximizing the triple bottom line subject to the equality and inequality constraints using the chemical complex analysis system. The optimal structure from the superstructure is shown in Fig. 2, and a convenient way to show the new plants in the optimal structure is given in Table 12. Seven new processes in the optimal structure were selected from 18 new processes in the superstructure. These included acetic acid, graphite, formic acid, methylamines, propylene (2) and synthesis gas production. The new acetic acid process replaced the commercial acetic acid plant in the chemical complex. The processes for dimethyl ether, styrene, and methanol were not selected in the optimal structure. It was more profitable to have the corresponding commercial processes present. The commercial process for methanol does not use expensive hydrogen as a raw material, but the new methanol processes do. A table showing the flow rates of all streams among the plants in the optimal structure is given by Indala 2004.

Comparison of the sales and costs associated with the triple bottom line, Eq. 6, are shown in Table 13 for the base case and the optimal structure. The triple bottom line increased from \$343 million per year to \$506 million per year or about 48% from the base case to the optimal structure. Sales increased from additional products from carbon dioxide, and there were corresponding increases in the other costs associated with producing these products by the companies. Cost to society improved since sustainable costs decreased from \$18 million per year to \$15 million per year from the credits given for using carbon dioxide and increased energy efficiency.

The increased use of carbon dioxide is shown in Table 14 for the optimal structure. However, it was not optimal to consume all of the carbon dioxide available, and 0.22 million metric tons per year is vented to the atmosphere, down from 0.61 million metric tons per year or 64%.

Six of the seven new processes present in the optimal structure use CO₂ as a raw material as shown in Tables 12 and 15. In Table 15, a comparison is given for

Table 11 Logical relations used to select the optimal structure

Logic expression	Logic meaning
$Y_{11} + Y_{12} \leq 1$	At most one of these two acetic acid plants is selected
$Y_{13} + Y_{14} \leq Y_3$	At most one of these two S and SO ₂ recovery plants is selected only if phosphoric acid (wet process) is selected
$Y_{16} + Y_{31} + Y_{32} + Y_{33} + Y_{34} \leq 1$	At most one of the five methanol plants is selected, the existing one or one of the four proposed plants
$Y_{11} \leq Y_{16} + Y_{31} + Y_{32} + Y_{33} + Y_{34}$	Only if at least one of these five methanol plants is selected, the conventional acetic acid may be selected
$Y_{35} + Y_{40} \leq Y_{41}$	At most one of these two styrene plants is selected only if ethylbenzene plant is selected
$Y_{29} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of the four plants that produce H ₂ is selected, the formic acid plant may be selected
$Y_{30} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of the four plants that produce H ₂ is selected, the methylamines plant may be selected
$Y_{31} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of the four plants that produce H ₂ is selected, the new methanol plant may be selected
$Y_{32} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of the four plants that produce H ₂ is selected, the new methanol plant may be selected
$Y_{33} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of the four plants that produce H ₂ is selected, the new methanol plant may be selected
$Y_{34} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of the four plants that produce H ₂ is selected, the new methanol plant may be selected
$Y_{37} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of the four plants that produce H ₂ is selected, the ethanol plant may be selected
$Y_{38} \leq Y_{23} + Y_{24} + Y_{27} + Y_{39}$	Only if at least one of the four plants that produce H ₂ is selected, the dimethyl ether plant may be selected

the production rates in the base case and the optimum structure for the plants in the chemical production complex. Also shown in this table are the energy used or produced for each process and the total energy required for the complex. With the additional plants in the optimal structure the energy required increased from 2,150 TJ/year to 5,791 TJ/year. This is reflected in the increased utility cost shown in Table 13 going from \$12 million per year to \$25 million per year. This additional energy is supplied from firing boilers with natural gas that has a sustainability cost of \$3.25 per metric ton. As shown in Table 15, the sulfuric acid plant is an important source of energy such as steam, and operating this plant for steam production is as important as production of sulfuric acid.

Two extensions to the optimal complex were evaluated. In one, the optimum was determined requiring that all of the CO₂ from the ammonia plant be consumed. In the other, the optimum was determined requiring that all of the CO₂ from the ammonia plant be consumed and the ammonia plant be operated at full capacity. These results are summarized in Table 16 along with the results in Tables 13 and 14. The triple bottom line decreased to \$467 million per year having consumed all of the CO₂ from the ammonia plant, and it decreased further to \$412 million per year with the additional requirement that the ammonia plant be operated at full capacity. These declines are a result of changes in sales and all of the associated costs as shown in Table 16.

A third extension had the sustainable credits be equal to the sustainable costs, \$3.25 per ton of carbon dioxide

rather than double, \$6.50 per ton. These results are shown in Table 16, and the sustainable costs increased from \$15 million per year to \$17 million per year as would be expected.

These case study results point out the need for methods that can give general evaluations. Results are needed to determine maximizing companies' profits and minimizing costs to society, and multicriteria optimization can provide this information. In addition, solutions are needed that incorporate the sensitivity of the optimal structure to prices and economic, environmental and sustainable costs; and Monte Carlo simulation is the appropriate procedure to generate these results. These methods have been applied, and the results are described in the next sections.

Application of multicriteria optimization

The objective is to find optimal solutions that maximize companies' profits and minimize costs to society. Companies' profits are sales minus economic and environmental costs. Economic costs include raw material, utilities, labor, and other manufacturing costs. Environmental costs include permits, monitoring of emissions, fines, etc. The costs to society are measured by sustainable costs. These costs are from damage to the environment by emissions discharged within permitted regulations. Sustainability credits are awarded for reductions in emissions by the amounts given in Table 10 and are similar to emissions trading credits.

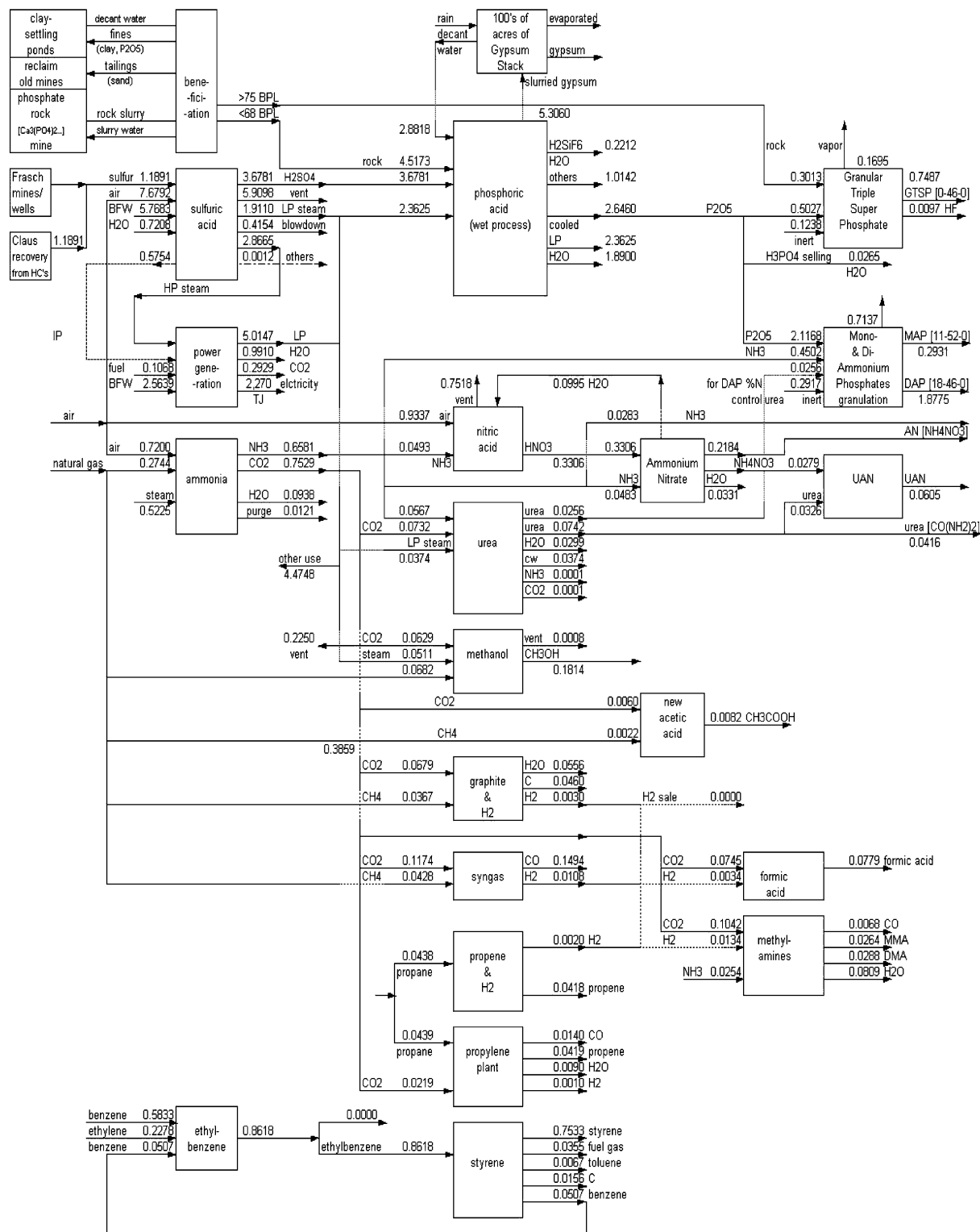


Fig. 2 Optimum configuration of the chemical production complex. Flow rates in million metric tons per year

The multicriteria optimization problem can be stated in terms of value-added profit, P , and sustainable credits/costs, S , for these two objectives as shown in Eq. 7.

$$\begin{aligned}
 \max : P &= \sum \text{product sales} - \sum \text{economic costs} \\
 &\quad - \sum \text{environmental costs} \\
 S &= \sum \text{sustainable (credits - costs)} \quad (7) \leftarrow
 \end{aligned}$$

Table 12 Plants in the optimal structure from the superstructure

Existing plants in the optimal structure	
Ammonia	
Nitric acid	
Ammonium nitrate	
Urea	
UAN	
Methanol	
Granular triple super phosphate (GTSP)	
MAP and DAP	
Contact process for sulfuric acid	
Wet process for phosphoric acid	
Ethylbenzene	
Styrene	
Power generation	
Existing plants not in the optimal structure	
Acetic acid	
New plants in the optimal structure	
Formic acid	
Acetic acid (new process)	
Methylamines (MMA and DMA)	
Graphite	
Hydrogen/synthesis gas	
Propylene from CO ₂	
Propylene from propane dehydrogenation	
New plants not in the optimal structure	
Methanol (Bonivardi et al. 1998)	
Methanol (Jun et al. 1998)	
Methanol (Ushikoshi et al. 1998)	
Methanol (Nerlov and Chorkendorff 1999)	
Ethanol	
Dimethyl ether	
Styrene (Mimura et al. 1998)	
Electric furnace process for phosphoric acid	
Haifa process for phosphoric acid	
SO ₂ recovery from gypsum waste	
S and SO ₂ recovery from gypsum waste	

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

Multicriteria optimization obtains solutions that are called efficient or Pareto optimal solutions. These are optimal points where attempting to improve the value of one objective would cause another objective to decrease. To locate Pareto optimal solutions, multicriteria optimization problems are converted to one with a single criterion by either of two methods. One is by applying weights to each objective and optimizing the sum of the

weighted objectives. The other is to convert the objectives to constraints, i.e., goal programming. The first method was used here, and the multicriteria mixed integer optimization problem becomes:

$$\max : w_1P + w_2S \quad (8)$$

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

The chemical complex analysis system was used to determine the Pareto optimal solutions for the weights using $w_1 + w_2 = 1$ given by Eq. 8, and these results are shown in Fig. 3. Companies' profits are an order of magnitude larger than sustainability credits/costs. Sustainability credits/costs decline and company profits increase as the weight, w_1 , on company profits increase. For example, when $w_1 = 1$, this is the optimal solution shown in Table 17 for $P = \$520.6$ million per year and $S = \$-14.76$ million per year. The optimal solution with $w_1 = 0$ gave $P = \$94.37$ million per year and $S = \$23.24$ million per year.

The points shown in Fig. 3 are the Pareto optimal solutions for w_1 from 0 to 1.0 for increments of 0.001. The values for w_1 equal to 0 and 1.0 and some intermediate ones are shown in Table 17. It shows that the sustainable costs become credits of \$0.68 million per year for a profit of \$389.8 million per year. Also, the optimal structure was affected, but it did not change significantly (Xu 2004). It is another decision to determine the specific value of the weight that is acceptable to all concerned.

Monte Carlo simulation

Monte Carlo simulation was used to determine the sensitivity of the optimal solution to the costs and prices used in the triple bottom line. One of the results 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 lesser than that value. This curve is used to determine upside and downside risks.

Table 13 Sales and costs associated with the triple bottom line for the base case and optimal structure

	Base case (million dollars per year)	Optimal structure (million dollars per year)
Income from sales	1,277	1,508
Economic costs (raw materials and utilities)	554	602
Raw material costs	542	577
Utility costs	12	25
Environmental cost (67% of raw material cost)	362	385
Sustainable credits (+)/costs (-)	-18	-15
Triple bottom line	343	506

Table 14 Carbon dioxide consumption in base case and optimal structure

	Base case (million metric tons per year)	Optimal structure (million metric tons per year)
CO ₂ produced by NH ₃ plant	0.75	0.75
CO ₂ consumed by methanol, urea and other plants	0.14	0.53
CO ₂ vented to atmosphere	0.61	0.22

For a Monte Carlo simulation, mean prices and costs along with an estimate of their standard deviations are required. The costs and prices in Table 10 were used, and standard deviations were estimated from cost and price fluctuations from the sources given in Table 10 over a 3- to 5-year period. These values are also given in

Table 10. Sustainable costs and credits were constant, and sensitivity to these values is to be determined in a subsequent evaluation. Monte Carlo simulations were run for a total of 1,000 iterations, and the cumulative probability distribution shown in Fig. 4 was obtained. The mean for the triple bottom line was \$513 million per year, and the standard deviation was \$109 million per year. For the 1,000 samples, the maximum was \$901 million per year, and the minimum was \$232 million per year. The triple bottom line from Table 13 is \$506 million per year, which is statistically the same as the mean for the Monte Carlo simulation, \$513 million per year.

Referring to Fig. 4, 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. For example from Fig. 8, there is 50% probability that the profit is equal to or less than \$513

Table 15 Comparison of production rates for the base case and optimal structure

Plant name	Production rate (upper-lower bounds) (mt/year)	Base case production rate (mt/year)	Energy requirement (TJ/year)	Optimal production rate (mt/year)	Energy requirement (TJ/year)
Ammonia	329,000–658,000	658,000	3,820	658,000	3,820
Nitric acid	89,000–178,000	178,000	–775	178,000	–775
Ammonium nitrate	113,000–227,000	227,000	229	227,000	229
Urea	49,900–99,800	99,800	128	99,800	128
Methanol	91,000–181,000	181,000	2,165	181,000	2,165
UAN	30,000–60,000	60,000	0	60,000	0
MAP	146,000–293,000	293,000		293,000	
DAP	939,000–1,880,000	1,880,000	1,901	1,880,000	1,901
GTSP	374,000–749,000	749,000	1,312	749,000	1,312
Sulfuric acid	1,810,000–3,620,000	3,620,000	–14,642	3,620,000	–14,642
Wet process phosphoric acid	635,000–1,270,000	1,270,000	5,181	1,270,000	5,181
Ethylbenzene	431,000–862,000	862,000	–755	862,000	–755
Styrene	386,000–771,000	753,000	3,318	753,000	3,318
Acetic acid	4,080–8,160	8,160	268	0	0
Electric furnace phosphoric acid	635,000–1,270,000	NA	NA	0	0
Haifa phosphoric acid	635,000–1,270,000	NA	NA	0	0
New Acetic acid	4,090–8,180	NA	NA	8,180	8
SO ₂ recovery from gypsum	987,000–1,970,000	NA	NA	0	0
S and SO ₂ recovery from gypsum	494,000–988,000	NA	NA	0	0
Graphite and H ₂ from CO ₂ and CH ₄	230,000–460,000	NA	NA	46,000	1,046
Syngas	6,700–13,400	NA	NA	10,800	691
Propene and H ₂	20,900–41,800	NA	NA	41,800	658
Propene using CO ₂	21,000–41,900	NA	NA	41,900	413
New Styrene	181,000–362,000	NA	NA	0	0
New methanol (Bonivardi et al. 1998)	240,000–480,000	NA	NA	0	0
New methanol (Jun 1998)	240,000–480,000	NA	NA	0	0
New methanol (Nerlov and Chorkendorff 1999)	240,000–480,000	NA	NA	0	0
New methanol (Ushikoshi et al. 1998)	240,000–480,000	NA	NA	0	0
Formic acid	39,000–78,000	NA	NA	78,000	14
Methylamines	13,200–26,400	NA	NA	26,400	1,079
Ethanol	52,000–104,000	NA	NA	0	0
Dimethyl ether	22,900–45,800	NA	NA	0	0
Ammonia sale		53,600		28,300	
Ammonium nitrate sale		218,000		218,000	
Urea sale		41,600		41,600	
Wet process phosphoric acid sale		12,700		12,700	
Ethylbenzene sale		0		0	
CO ₂ vented		612,000		225,000	
Total energy requirement			2,150		5,791

NA not available

Table 16 Results for base case, optimal structure and extensions

	Base case	Optimal	Use all CO ₂	Max NH ₃ plant	Equal CO ₂ credit and cost
Income from sales (million dollars per year)	1,277	1,508	1,392	1,174	1,508
Economic costs (raw materials and utilities) (million dollars per year)	554	602	560	460	602
Raw material costs (million dollars per year)	542	577	533	435	577
Utility cost (million dollars per year)	12	25	27	25	25
Environmental cost (67% of raw material cost; million dollars per year)	362	385	355	290	385
Sustainable credits (+)/costs(-) (million dollars per year)	-18	-15	-10	-12	-17
Triple bottom line (million dollars per year)	343	506	467	412	504
CO ₂ produced by NH ₃ plant (Million metrictons per year)	0.75	0.75	0.56	0.75	0.75
CO ₂ consumed by methanol, urea and other plants (Million metrictons per year)	0.14	0.53	0.56	0.75	0.53
CO ₂ vented to atmosphere (Million metrictons per year)	0.61	0.22	0.0	0.0	0.22

million per year. Now a range of values is available for the optimum triple bottom line that can be used to assess the risk of proceeding as measured by the cumulative probability distribution. Also, the optimal structure was affected, but it did not change significantly (Xu 2004).

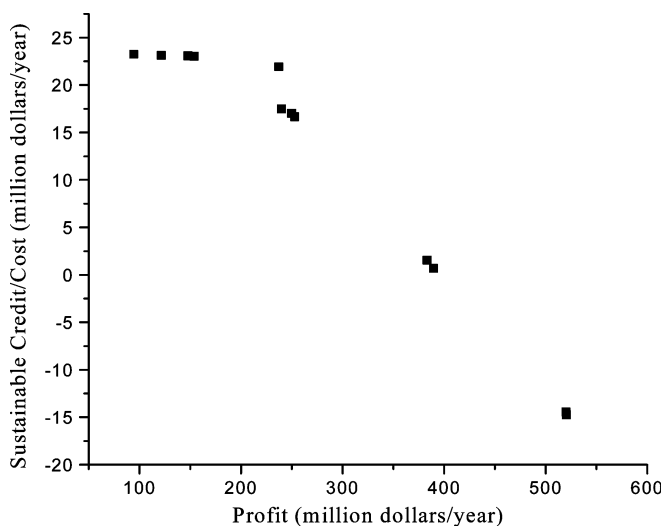
Conclusions

Fourteen new energy-efficient and environmentally acceptable catalytic processes have been identified that can use excess high-purity carbon dioxide as a raw material from ammonia plants and other sources available in a chemical production complex. The chemical production complex in the lower Mississippi River corridor has been used to show how these new plants can be integrated into this existing infrastructure using the chemical complex analysis system.

Eighty-six published articles of laboratory and pilot plant experiments were reviewed that describe new

methods and catalysts to use carbon dioxide for producing commercially important products. Reactions have been categorized as hydrogenation reactions producing alcohols; hydrocarbon synthesis reactions producing paraffins and olefins; amine syntheses producing methyl and higher order amines; and hydrolysis reactions producing alcohols and organic acids. Also carbon dioxide can serve as an oxygen source in the ethyl benzene-to-styrene reaction, and it can be used in dehydrogenation and reforming reactions.

A methodology for selecting the new energy-efficient processes was developed. The selection criteria included: process operating conditions, energy requirement for reactions, ΔH_E ; thermodynamic feasibility and equilibrium conversion of the reactions based on Gibbs free energy change, ΔG_E ; catalyst conversion, selectivity, cost and life (time onstream 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 and sustainable costs were evaluated along with hydrogen consumption for hydrogenation reactions.

**Fig. 3** Optimal solutions generated by multicriteria optimization**Table 17** Several values of the pareto optimal solutions shown in Fig. 3

Profit (million dollars per year)	Sustainable credits/costs (million dollars per year)	Weight (w_1)
520.6	-14.76	1
520.1	-14.45	0.417
389.8	0.68	0.172
383.1	1.53	0.115
252.9	16.68	0.104
249.8	17.02	0.103
239.7	17.48	0.039
237.1	21.93	0.037
153.7	23.04	0.013
147.6	23.07	0.004
121.5	23.12	0.002
94.37	23.24	0

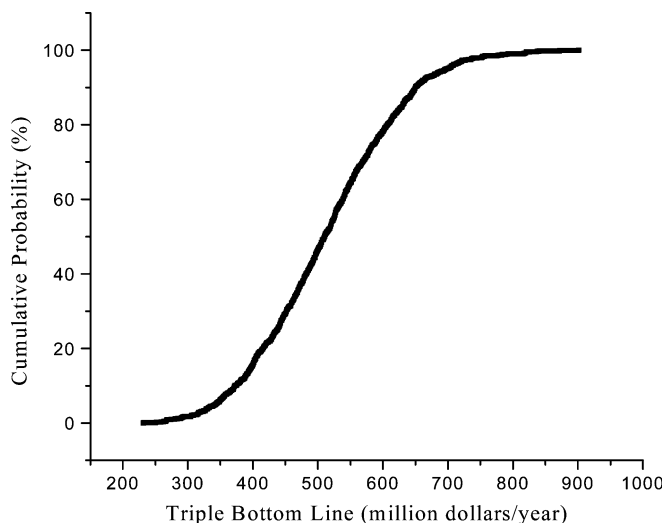


Fig. 4 Cumulative probability distribution for the triple bottom line of the optimal structure

Based on the methodology for selecting new processes, 20 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. From these, 14 of the most promising were integrated in a superstructure that included plants in the existing chemical production complex in the lower Mississippi River corridor (base case). These processes include production of methanol, ethanol, dimethyl ether, propylene, formic acid, acetic acid, styrene, methylamines, graphite, and synthesis gas. The base case of existing plants in the chemical production complex in the lower Mississippi river corridor included 13 multiple plant production units plus associated utilities for power, steam and cooling water and facilities for waste treatment.

The optimum configuration of plants was determined based on economic, environmental and sustainable costs using the chemical complex analysis system. From 18 new processes in the superstructure, the system selected seven new processes in the optimal structure. These included acetic acid, graphite, formic acid, methylamines, propylene (2) and synthesis gas production. With the additional plants in the optimal structure the profit (triple bottom line) increased from \$343 million per year to \$506 million per year and energy use increased from 2,150 TJ/year to 5,791 TJ/year.

Three extensions to the optimal complex were evaluated. In one, the optimum configuration of plants was determined requiring that all of the CO_2 from the ammonia plant be consumed. In the second, the optimum configuration of plants was determined requiring that all of the CO_2 from the ammonia plant be consumed and that the ammonia plant be operated at full capacity. The triple bottom line decreased to \$467 million per year having consumed all of the CO_2 from the

ammonia plant, and it decreased further to \$412 million per year with the additional requirement that the ammonia plant be operated at full capacity. These declines are a result of changes in sales and all of the associated costs. A third extension had the sustainable credits equal to the sustainable costs, \$3.25 per ton of carbon dioxide rather than double, \$6.50 per ton. The sustainable costs increased from \$15 million per year to \$17 million per year as would be expected.

The chemical complex analysis system was used for multicriteria optimization to find optimal solutions that maximize companies' profits and minimize costs to society, called efficient or Pareto optimal solutions. These are optimal points where attempting to improve the value of one objective would cause another objective to decrease. Companies' value-added profits are sales minus economic and environmental costs. Economic costs included here were raw material and energy costs. Environmental costs include permits, monitoring of emissions, fines, etc. The costs to society are measured by sustainable costs. These costs are from damage to the environment by emissions discharged within permitted regulations. When only maximizing companies' profits, the optimal solution was \$520.6 million per year for companies' profit and sustainable credits/costs were \$-14.76 million per year. When only maximizing sustainable credits/costs the optimal solution was \$94.37 million per year for companies' profit and sustainable credits were \$23.24 million per year. One of the intermediate optimal values was a profit of \$389.8 million per year and sustainable credits of \$0.68 million per year. It is another decision to determine the specific value of the weight that is acceptable to all concerned.

Monte Carlo simulation was used to determine the sensitivity of the optimal solution to the costs and prices for the chemical production complex triple bottom line model with the cumulative probability distribution, a curve of the probability as a function of the triple bottom line. Costs, prices and standard deviations were estimated from cost and price fluctuations for the last five years. A total of 1,000 iterations were used, and the mean profitability was \$513 million per year, which is essentially the same value that was obtained for the optimal structure of \$506 million per year. The standard deviation was \$109 million per year, and for 1,000 samples, the maximum was \$901 million per year, and the minimum was \$232 million per year. Now a range of values is available for the optimum triple bottom line that can be used to assess the risk of proceeding as measured by the cumulative probability distribution. Sustainable costs and credits were constant, and sensitivity to these values is to be determined in a subsequent evaluation.

Multicriteria optimization has been used with Monte Carlo simulation to determine the sensitivity of prices, costs, and sustainability credits/cost to the optimal structure of a chemical production complex. In essence, for each Pareto optimal solution, there is a cumulative

probability distribution function that is the probability as a function of the triple bottom line. This information provides a quantitative assessment of the optimum profit versus sustainable credits/cost, and the risk (probability) that the triple bottom line will meet expectations.

The capabilities of the chemical complex analysis system have been demonstrated by determining the optimal configuration of units based on economic, environmental and sustainable costs. Based on these results, the methodology could be applied to other chemical complexes in the world for reduced emissions and energy savings. The system was developed by industry–university collaboration, and the program with users manual and tutorial can be downloaded at no cost from the LSU Mineral Processing Research Institute's website <http://www.mpri.lsu.edu>. Also, all of the HYSYS simulations described here and the chemical complex analysis program and users manual are available on the web site.

Future research

The methodology presented here can be applied to other sources of carbon dioxide. For example, flue gases from gas-fired turbines have 3.0 mol % CO₂ and coal-fired plants have 10–12% CO₂ (Freguia et al. 2003). The standard process of amine scrubbing gives essentially pure CO₂ from flue gases, and costs range from \$50 per ton to \$60 per ton of CO₂ captured (Simmonds et al. 2002). Research is described by Ondrey (2003) for new, more efficient methods to remove carbon dioxide from combustion gases.

Potential processes for fullerenes and carbon nanotubes can be designed based on laboratory experimental studies that are available in the literature as were done for carbon dioxide. For example, laboratory catalytic reactors are used to produce gram quantities of carbon nanotubes, and batch purification involves removing impurities with strong mineral acids. These new processes could be high temperature, energy intensive and hazardous waste generating processes. They could be designed using the advanced process analysis system available from the Minerals Processing Research Institute's web site <http://www.mpri.lsu.edu>. Then these process designs could be used with the chemical complex analysis system to evaluate integrating these new processes into the existing infrastructure of plants and determine the best energy-efficient and environmentally acceptable processes.

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