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A prototype system for economic, environmental and sustainable optimization of a chemical complex

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Abstract A prototype of a chemical complex analysis system has been developed and used to demonstrate optimization of a chemical complex. The system incorporates economic, environmental and sustainable costs, and solves a MINLP for the best configuration of plants. It was applied to expanding production of sulfuric and phosphoric acid capacities and to evaluating heat recovery options at a major chemical company, and the results were compared to the company's case study. The system selected the better of two sites for required new phosphoric and sulfuric acids production capacities and selected, sited, and sized the optional heat-recovery and power-generation facilities. System capability was demonstrated by duplicating and expanding the industrial case study. A second application of the prototype was based on an agricultural chemical complex with ten multiple plant production units as found in the Baton Rouge–New Orleans, Mississippi river corri-

liability costs. Type 4 costs are internal intangible costs, and Type 5 costs are external costs that the company does not pay directly including those borne by society and from deterioration of the environment by pollution within compliance regulations. This report states that environmental costs made up at least 22% of the nonfeedstock operating costs of the Amoco's Yorktown oil refinery. Also, for one DuPont pesticide, environmental costs were 19% of the total manufacturing costs; and for one Novartis additive these costs were a minimum of 19% of manufacturing costs, excluding raw materials. In addition, this TCA methodology was said to have the capability to evaluate the full life cycle and consider environmental and health implications from raw material extraction to end-of-life of the process or product.

Sustainable development is the concept that development should meet the needs of the present without sacrificing the ability of the future to meet its needs. There have been many publications on sustainable development and environmental economics, which are described by Daly (1996), and in 1995 the President's Council on Sustainable Development issued a report giving 15 principles. These included calls to preserve the integrity of natural systems; to have economic growth, environmental protection and social equity be interdependent; to have a stable population consistent with the carrying capacity of the Earth; and to have all segments of society equitability share environmental costs. How these principles will be considered and ways to proceed involve complex political, trade, health, scientific and technical issues. Approaches have been and are being proposed by economists, government officials and business leaders. First, measures or metrics of sustainable development must be defined, tested and applied before sound policy decisions can be proposed and evaluated. An effort is underway to develop these metrics by an industry group through the Center for Waste Reduction of the American Institute of Chemical Engineers, and they have issued two interim reports (Adler 1999) and held a workshop (Beaver and Beloff 2000). Also, external or sustainable costs are the very difficult to quantify, and the TCA report gives some estimates for these costs from a study of environmental cost from pollutant discharge to air from electricity generation, e.g. U.S.$0.22–2.38 per ton for CO, U.S.$0–3.25 per ton for CO_2.

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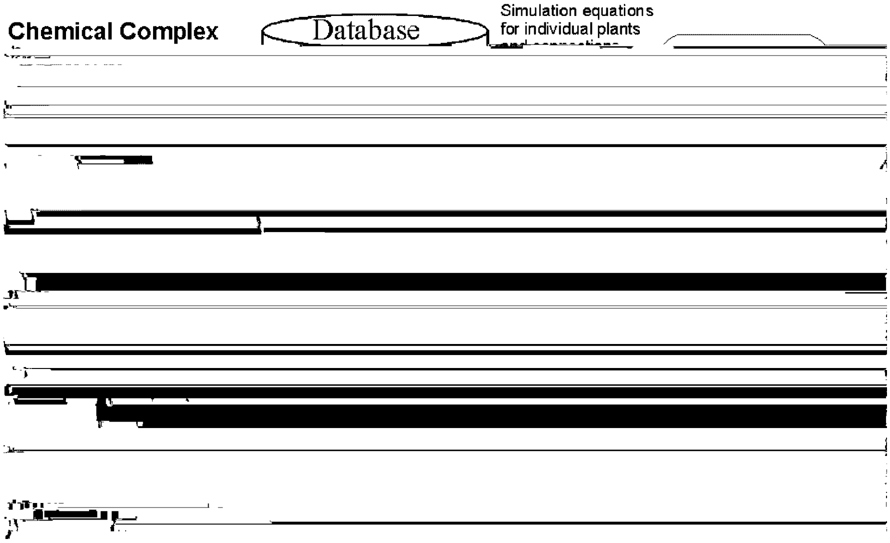
A prototype system shown in Fig. 1 has been developed that combines components to determine the optimum configuration of plants in a chemical complex. Economic, environmental and sustainability costs are combined in the objective function to be optimized. The constraints include the material and energy balances, rate equations and equilibrium that describe the performance of the individual plants and how they are connected. Also included in the model of the complex are the equations that give the demand for product, availability of raw materials and capacity ranges for the plants. This formulation is a mixed integer nonlinear programming problem (MINLP), and the GAMS and SYNPHONY solvers are used to determine the optimal configuration from the superstructure of plants developed from a base case of existing plants.

The system has been developed in collaboration with engineering groups at Monsanto Enviro Chem, Motiva Enterprises, IMC Agrico and Kaiser Aluminum and Chemicals to ensure it meets the needs of the chemical and petroleum refining industries. The prototype incorporates TCA methodology from the AIChE/CWRT Total Cost Assessment Methodology (Constable et al. 2000).

The System is designed for use by corporate engineering groups who have to convert their company's goals and capital into viable projects that are profitable and meet environmental and sustainability requirements and have to perform evaluations for impacts associated with greenhouse gases, finite resources etc. This program can be used with these projects and evaluations and also can help demonstrate that plants are delivering environmental, social and business benefits that will help ameliorate command and control regulations.

As shown in Fig. 1, the Chemical Complex Analysis System incorporates a flowsheeting component where the simulations of the plants in the complex are entered. Individual processes can be drawn on the flowsheet using a graphics program. The plants are connected in the flowsheet as shown in Fig. 2. For each process, material and energy balances, rate equations, equilibrium relations and thermodynamic and transport properties are entered through windows and stored in an Access database to be shared with the other components of the system. Also, the objective function is entered as an equation associated with each process with related information for prices and economic, environmental and sustainable costs that are used in the evaluation of the TCA for the complex. The TCA includes the total profit for the complex that is a function of the economic, environmental and sustainable costs and income from sales of products. Then the information is provided to either GAMS/DICOPT or SYNPHONY for solving the MINLP problem for the optimum configuration of plants in the complex. Also, sources of pollutant generation are located by the pollution index component of the system using the EPA pollution index methodology (Cabezas et al. 1997).

All interactions with the system are through the graphical user interface that is written in Visual Basic. Referring to the left side of Fig. 1, as the process flow diagram for the complex is prepared, equations for the process units and variables for the streams connecting the process units are entered and stored in the database using interactive data forms. Material and energy balances, rate equations and equilibrium relations for the plants are entered as equality constraints using the format of the GAMPt to enteiuag4(for)-9.2(b85(is)-102.5(a)]TJT89.5(omilar)-102.58



As described above, the TCA report includes an Excel spreadsheet with an extensive listing of five types of costs. The prototype combines these five categories of costs into three costs: economic, environmental and sustainable. Types 1 and 2 are included in economic costs, Types 3 and 4 are included in environmental costs, and Type 5 is sustainable costs. Economic costs are estimated by standard methods (Garrett 1989). Environmental costs are estimated from the data provided by Amoco, DuPont and Novartis in the AIChE/CWRT report. Sustainable costs are estimated by the study of power generation in this report. It is an on-going effort to refine and update better estimates for these costs.

As shown in Fig. 1, the system will provide an option to select one of two optimization methods. GAMS/DCOPT and SYNPHONY. GAMS (General Algebraic Modeling System) was developed at the World Bank for very large economic models, and it can be used to determine the optimal configuration of a chemical complex by solving a MINLP programming problem using the DICOPT solver (Kocis and Grossmann 1989). SYNPHONY uses process graph methodology based on the work of Friedler and Fan (Friedler et al. 1995) to solve the MINLP problem.

After determining the optimal complex configuration, the pollution index part of the system is called to perform a pollution prevention analysis. It reads all the necessary stream information from the database. Additional data such as specific environmental impact potentials and weighting factors are supplied. These results are presented to the user for evaluation and stored in the database for subsequent retrieval. The EPA pollution index and potential environmental impact methodology (Cabezas et al. 1997) provides a quantitative way to identify pollutants and their potential impacts from the complex. There are four physical potential impacts (acidification, greenhouse enhancement, ozone depletion and photochemical oxidant formation), three human toxicity effects (air, water and soil) and two ecotoxicity effects (aquatic and terrestrial). The pollution impact of a process is useful in determining

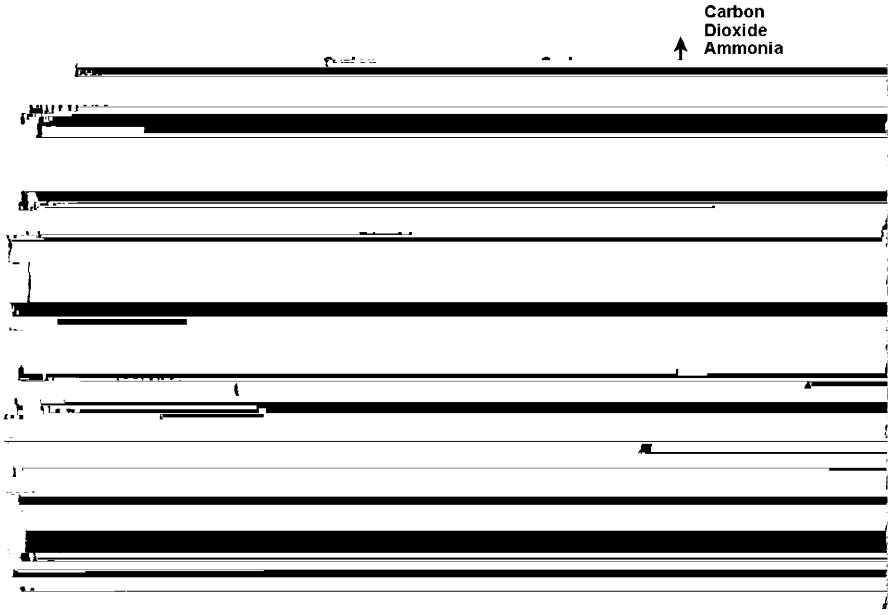


Fig. 2. Schematic diagram of agricultural chemicals complex with raw materials, products, emissions and wastes

the second; and a second sulfuric acid expansion does not have to be sited away from the first expansion. Also, there are options for adding heat recovery equipment to one old and any new sulfuric plants and for adding one turbogenerator per site per stage.

Based on the description above, a superstructure was developed that had 67 components [600 psig (4.24 MPa) steam, sulfuric acid, logic switches etc.] and 75 processing units. The detailed description process models and superstructure formulation was given by Hertwig et al. (2000). The superstructure was entered in the prototype, and SYNPHONY was used as the solver. Computing time for any one case was less than 15 s on a Pentium II PC. Results obtained with the system were consistent with the case studies done previously by the company. This served to validate that the system was giving consistent and accurate results. A summary of the evaluations includes raising the cost of shipping sulfuric acid between sites; the sites could be forced to be self-sufficient in sulfuric production capacity. This impacted steam- and power-generation capacities at each site. Also, production rate for a higher-emissions, single absorption sulfuric acid plant was curtailed as expected by voluntarily limiting the two-site SO_2 emissions to pre-expansion levels. With this old plant curtailment, the new sulfuric plant was built with corresponding extra capacity. The curtailed, single-absorption sulfuric plant was converted to double-absorption for expansion at stage two when the conversion cost was significantly less than the cost of a new plant.

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Blau and Kuenker of Dow AgroScience (Blau and Kuenker 1998) reported that delivering nutrients to the various crops rather than focusing on production of fertilizers would lead to the best overall economic, environmental and sustainable development solutions for agricultural chemicals. This statement provides direction for use of the prototype system. The system should help determine the best way to make key nutrients of N, P and K available to crops where and when most needed.

An agricultural chemical complex based on plants in the Baton Rouge–New Orleans, Mississippi river corridor was developed with information provided by the cooperating companies and other published sources, as shown in Fig. 3. This complex is representative of the current operations and practices in the agricultural chemical industry and was used as the base case and starting point to develop a superstructure by adding plants. These additional plants gave alternative ways to produce intermediates that reduced and consumed wastes and greenhouse gases and conserved energy. These additional plants could provide combinations leading to a complex with lower environmental impacts and greater sustainability. Then this superstructure wasTnr61.

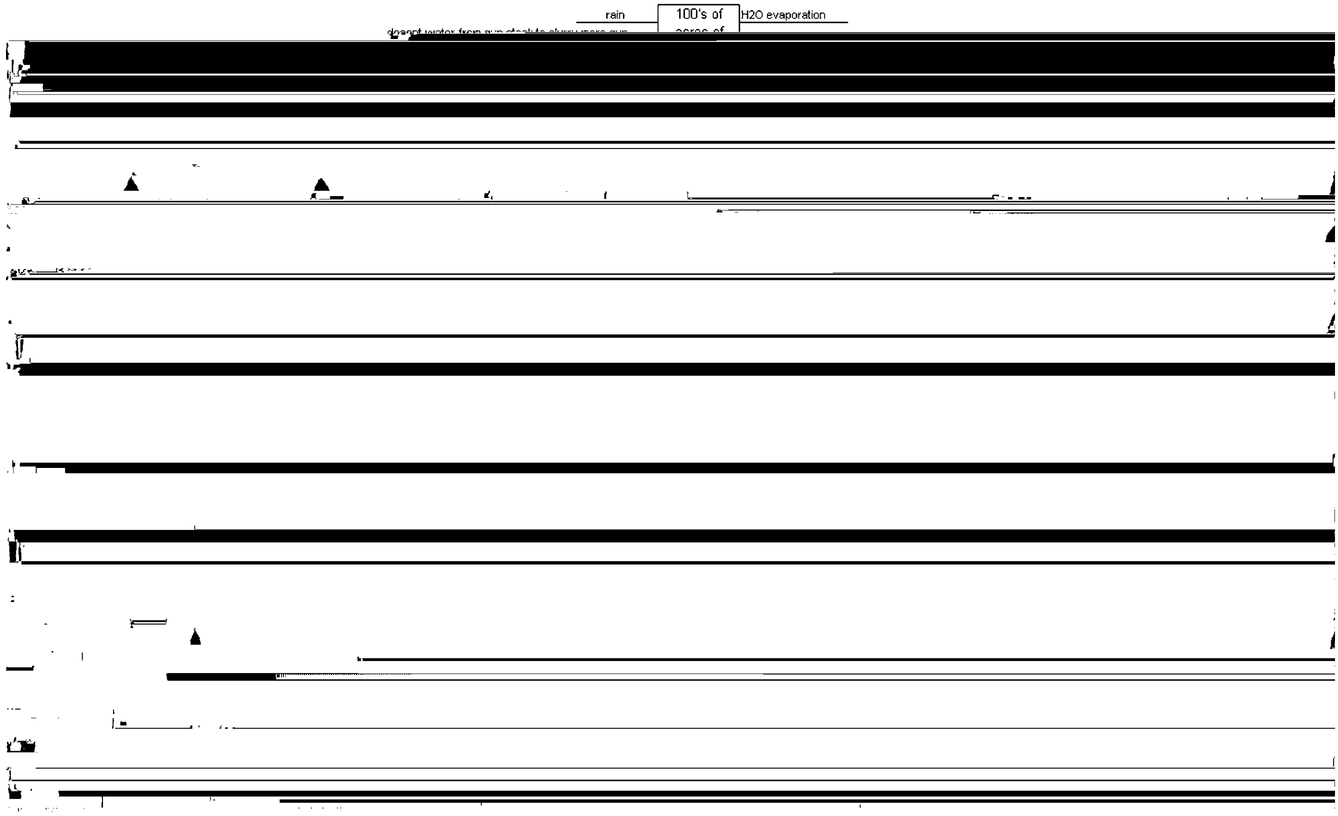

Fig. 3. Agricultural chemical complex based on plants in the Baton Rouge–New Orleans, Mississippi river corridor, base case flow rates million t/year

million tons per year. Intermediates are sulfuric acid, phosphoric acid, ammonia, nitric acid, urea and carbon dioxide. The intermediates are used to produce mono- and di-ammonium phosphate (MAP and DAP), granular triple super phosphate (GTSP), urea, ammonium nitrate, and urea ammonium nitrate solution (UAN). These compounds are used to make blends shown in Fig. 3. Their pre-blending compositions are: MAP [11–52–0], DAP [18–46–0], GTSP [0–46–0], urea ($CO(NH_2)_2$) [46–0–0], ammonium nitrate [34–0–0], and UAN [$\sim$30–0–0]. Also, potassium supplied as potassium chloride for blends is not produced on the Gulf coast but is imported from New Mexico and Utah, among other states. Ammonia is used in direct application to crops and other uses. Methanol is used to produce formaldehyde, methyl esters, amines and solvents, among others, and is included for its use of ammonia plant byproduct carbon dioxide. In actual practice several blends are produced, and they would just add blending constraints to the base case.

Emissions from an agricultural chemical complex include sulfur dioxide, nitrogen oxides, ammonia, methanol, silicon tetrafluoride, hydrogen fluoride and gypsum. According to EPA 1996 TRI (Anon 1998) Louisiana's four chemicals for on- and off-site releases are phosphoric acid, ammonia, methanol and nitrate compounds in Louisiana. The total on- and off-site releases in the state were 29.7 (13.5), 27.7 (12.6), 25.2 (11.4) and 14.5 (6.6) million pounds (Gg) in 1996. Phosphoric acid plants had 28.3 million pounds (12.8 Gg) of surface water discharges from gypsum waste. Ammonia plants had 21.6 million pounds (9.8 Gg) of air emissions. Methanol plants had 17.1 million pounds (7.8 Gg) of air emissions and 7.1 million pounds (3.2 Gg) of underground injection. Plants producing nitrate compounds had 8.4 (3.8) and 6.0 (2.7) million pounds (Gg) of surface water and underground injection, respectively.

The agricultural chemical complex shown in Fig. 3 was expanded into a superstructure, and several approaches were incorporated in this expanded complex with alternative ways to produce intermediates that reduce wastes and energy and consume greenhouse gases. There were two alternative plants added to produce phosphoric acid. One was the electric furnace process, which has high energy costs but produces calcium oxide. The other reacts calcium phosphate ore with HCl to produce phosphoric acid with dissolved calcium chloride that is dispersed with the product versus gypsum (calcium sulfate) waste that accumulates adjacent to the phosphoric acid plant. Also, phosphoric acid and sulfuric acid can be purchased from other sources such as smelters. Potassium chloride can be purchased directly from plants using the Trona, IMCC and sylvinite ore processes and can be purchased from suppliers or dealers. An ammonium sulfate plant was included to provide an additional blending component. An acetic acid plant was included that would use a new/experimental technology for the catalytic reaction of carbon dioxide and methane, consuming two greenhouse gases. Carbon dioxide, beyond amounts required in the methanol plant, was used to produce acetic acid, a new product for the complex. In summary, the superstructure included four options for producing/buying each of phosphoric acid and

Table 1. Raw material and product prices (U.S.$/t). Source Green Market Sheet (10 July 2000), Internet and AIChE/CWTR TCA Report

Raw materials	Cost (U.S.$/t)	Raw materials	Cost (U.S.$/t)	Raw materials	Cost (U.S.$/t)
Natural gas	40	Market cost for short term purchase		Ammonia	190
Phoshate rock				Methanol	96
wetprocess	27			Acetic acid	45
electrofurnace	24	KCI	101	Solid blend	160
HCI process	25	H3PO4	176	Liquid blend	60
HCI	50	H2SO4	86	HP steam	10
Sulfur				IP steam	64
Frasch	42	Sustainability credits and costs (U.S.$/t)			
Claus	38	Credit for CO_2 consumption			6.50
Brine KCl ore	2				
Searles Lake KCl ore	15	Debit for CO_2 production			3.25
Sylvinite KCl ore	45				

potassium chloride, two options for sulfuric acid, and new plants to produce ammonium sulfate and acetic acid. The block flow diagram and associated equations for the superstructure are given by Xu et al. (2001) in the program and users manual. The superstructure had 265 continuous variables, 10 integer variables, 232 equality constraint equations for material and energy balances and 37 inequality constraints for availability of raw materials, demand for product and capacities of the plants in the complex.

A value added economic model was used for the base case, and it is the difference between sales and the cost of raw materials and assumes other manufacturing costs are constant. The sales prices for products and costs of raw materials are given in Table 1. For the superstructure, the economic model was expanded to account for environmental and sustainability costs. Environmental costs were estimated as 67% of the raw material costs, which is based on the data provided by Amoco, DuPont and Novartis in the AIChE/CRWRT report (Constable et al. 2000). This report lists environmental costs as approximately 20% of the total manufacturing costs and raw material costs as approximately 30% of total manufacturing costs. Sustainable costs were estimated from results given for power generation in the AIChE/CWRT report where carbon dioxide emissions had a sustainable cost of U.S.$3.25 per ton of carbon dioxide. A cost of U.S.$3.25 per ton was charged as a cost to plants that emit carbon dioxide, and plants that consume carbon dioxide were given a credit of twice this cost or U.S.$6.50 per ton. This credit was included for steam produced from waste heat by the sulfuric acid plant displacing steam produced from a package boiler firing hydrocarbons and emitting carbon dioxide.

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Table 2. Comparision of base case and optimal structure

Profit (U.S.$/year) Environmental cost (U.S.$/year) Sustainability cost (U.S.$/year) Plant name	Capacity (t/year) (upper–lower bounds)	Base case 1,691,235,000 (295,040,000) 26,880,000 Capacity (t/year)	Optimal structure 1,823,000,000 (244,120,000) 27,308,000 Capacity (t/year)
Ammonia			
Nitric acid			
Ammonium nitrate			
Urea			
Methanol			
UAN			

Conclusions

A prototype of a chemical complex analysis system has been described, and its capability was demonstrated by duplicating and expanding an industrial case study. The system selected the best site for required new phosphoric and sulfuric acids production capacities and selected, sited and sized the optional heat-recovery and power-generation facilities. A second application of the prototype was based on an agricultural chemical complex with ten multiple plant production units in the Baton Rouge–New Orleans, Mississippi river corridor. The optimal configuration of plants was determined based on economic, environmental and sustainable costs. A comparison of the current configuration of units with the optimal one was made and sensitivity to cost and prices was analyzed. The profit increased about 7.8% from the base case to the optimal solution. Also, environmental cost declined about 17%, and sustainability costs increased about 1.5%. These results illustrated the capability of the system to select an optimum configuration of plants in an agricultural chemical complex and incorporate economic, environmental and sustainable costs. A brief sensitivity study gave predictable results and demonstrated additional capabilities of the system.

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