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Developing and Integrating Sustainable Chemical Processes into Existing Petro-Chemical Plant Complexes

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Abstract

A wide variety of industrial chemicals can be produced from biomass feedstock that are produced from petroleum based feedstock. The chemical production complex of existing plants in the lower Mississippi River corridor is a base case of existing plants. New plants that use biomass as raw materials are integrated into the base case and include a transesterification process, a fermentation process and anaerobic digestion process. Other plants include gasification and pyrolysis as well as Fishcher Tropsch synthesis. Raw materials include algae, corn, sugarcane, soybeans or from waste biomass like corn stover, bagasse, and municipal solid waste. Products include polymers from fatty acid esters, propylene glycol and 1,3-propanediol from glycerin, ethylene and ethylene derivatives from biobased ethanol, acetic acid from anaerobic digestion. The Chemical Complex Analysis System is used to determine the best configuration of plants in a chemical complex based on economic, energy, environmental and sustainable costs. It incorporates a flowsheeting component where simulations of the plants in the complex are entered. Each simulation includes the process or block flow diagram with material and energy balances, rate equations, equilibrium relations and thermodynamic and transport properties for the process units and heat exchanger networks. Multi-criteria optimization is used with Monte Carlo simulation to determine the optimal configuration of plants in chemical production complex and sensitivity to prices, costs and sustainability credits/costs. Results from using the System had soybean and algae oil going from the transesterification process into polyurethane foams and propylene glycol. Ethanol from fermentation goes into the ethylene chain to produce polyethylene. Anaerobic digestion provides acetic acid and cellulose acetate. Gasification, pyrolysis and Fishcher Tropsch synthesis were not in the configuration of plants in the optimal structure.

Introduction

Global warming, biotechnology and nanotechnology are on a collision course because new processes for carbon nanotubes and chemicals from biomass are energy intensive and generate carbon dioxide. Industrial processes that use biomass and carbon dioxide as raw materials are an important option in mitigating the effects of global warming. The objectives of this research are to identify and design new industrial processes that use biomass as raw materials and show how these processes could be integrated into existing chemical production complexes. The research demonstrates how existing plants can transition to renewable feedstocks from nonrenewable feedstocks. A wide variety of industrial chemicals can be produced from biomass feedstock that are produced from petroleum based feedstock.

Chemical Production Complex – Base Case

The chemical production complex of existing plants in the lower Mississippi River corridor is a base case of existing plants. A map of the plants in the lower Mississippi River corridor is shown in Figure 1. There are about 150 chemical plants produce a wide range of petrochemical that are used in housing, automobiles, fertilizer and numerous other consumer products, consuming 1.0 quad (10^{15} BTUs per year) of energy (Peterson, 2000).

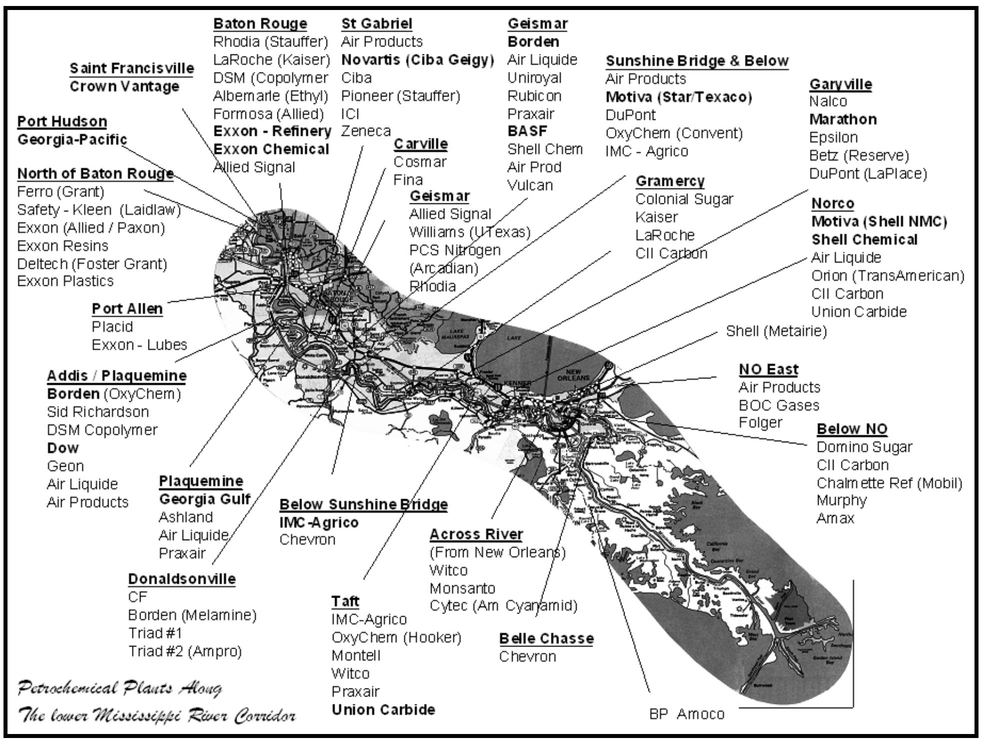

Figure 1: Plants in the Lower Mississippi River Corridor (Peterson, 2000)

In Figure 2, a chemical production complex was developed with the assistance of industrial collaborators and other published sources. It is based on the plants in the agricultural chemical chain and the methanol and benzene chains in the lower Mississippi river corridor. This complex is representative of current operations and practices in the chemical industry and is called the base case of the existing plants. It includes the sources and consumers of carbon dioxide in the chemical production complex. This description of the chemical production complex was used in research on carbon dioxide utilization and is now being used in research on chemical production from biomass feedstock, carbon nanotubes production and energy integration.

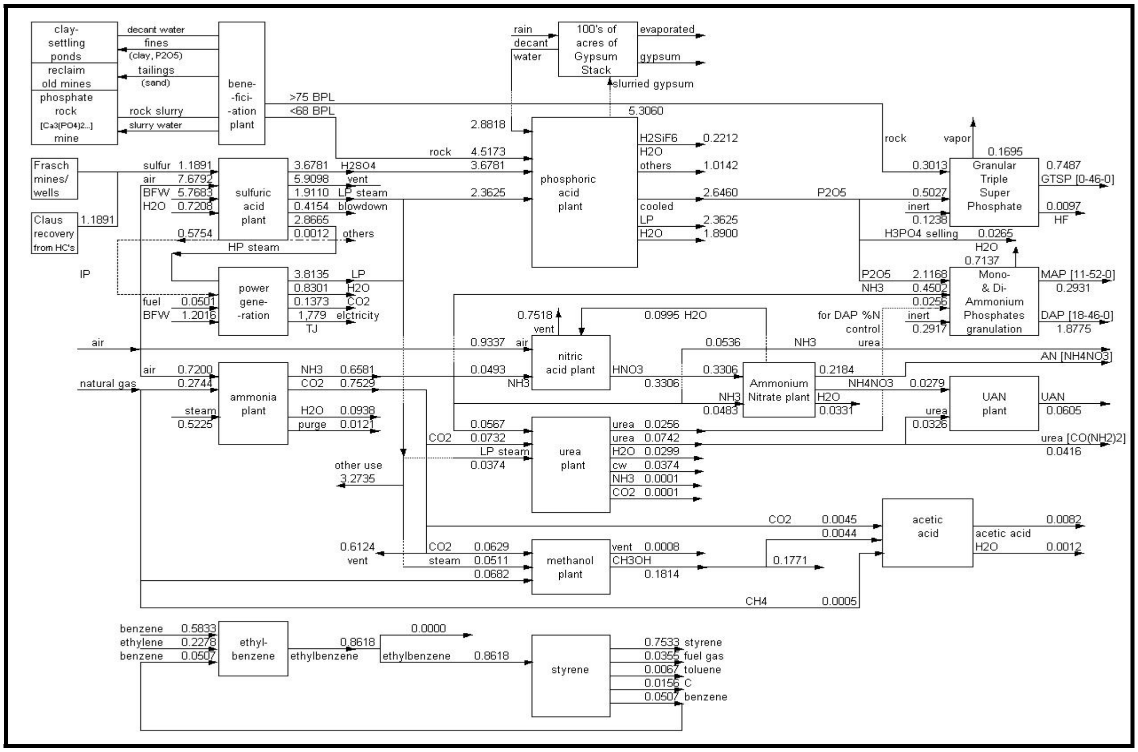

Figure 2: Chemical Production Complex in the Lower Mississippi River Corridor, Base Case, Flow Rates - Million Metric Tons per Year (Xu, 2004)

As shown in Figure 2 this chemical production complex has thirteen production units plus associated utilities for power, steam and cooling water and facilities for waste treatment. A production unit contains one plant. The phosphoric acid production unit contains four plants owned by three companies. The sulfuric acid production unit contains five plants owned by two companies (Hertwig, 2004). 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 that is now being vented to the atmosphere.

Chemical Production Complex – Super Structure

New plants that use biomass as raw materials are integrated into the base case to form a super structure of chemical plants. These new processes include a transesterification process, a fermentation process and anaerobic digestion process. Other plants include gasification and pyrolysis as well as Fishcher Tropsch synthesis. The setup for new chemical plants from biomass feedstock using the above processes is shown in Figure 3.

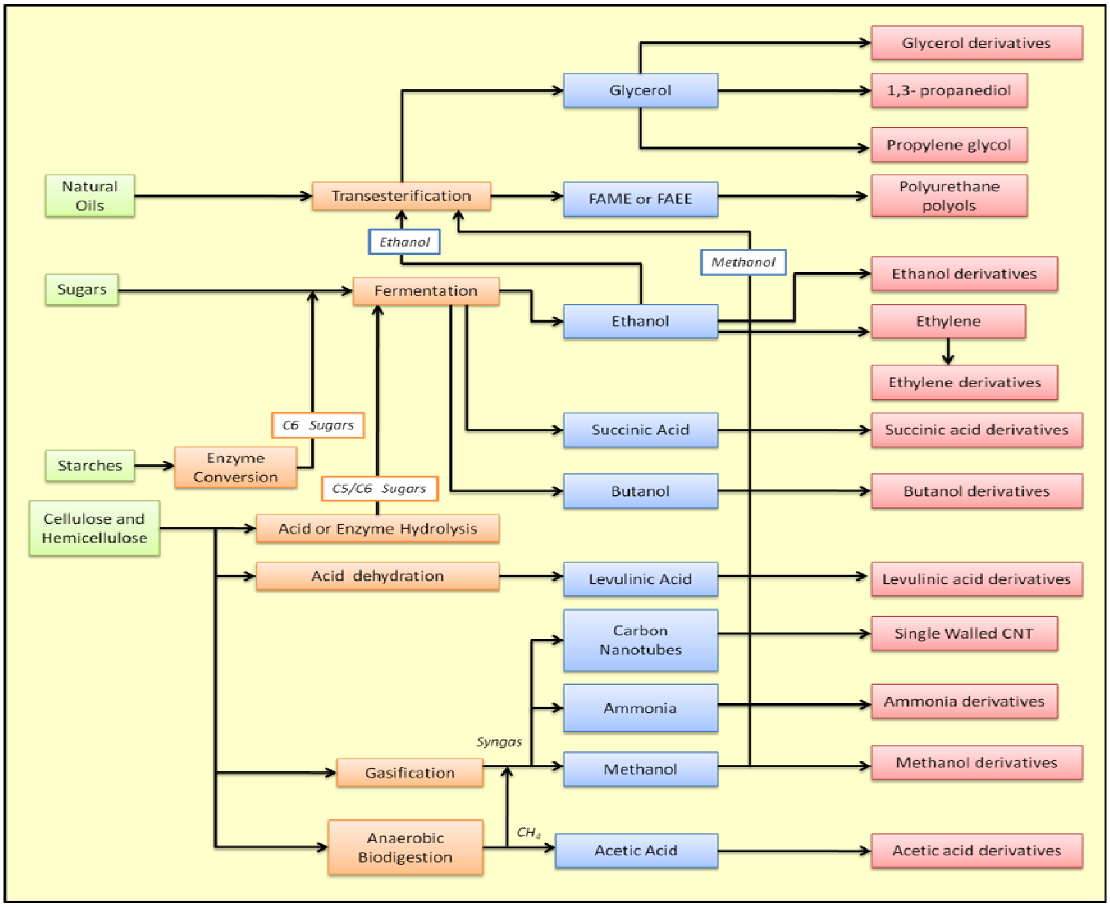

Figure 3: Proposed Biomass Based Complex Extension with Single-Wall Carbon Nanotube Production

The vision is to convert industries based on non-renewable resources to ones based on renewable resources. The initial evaluation will be the introduction of ethanol into the ethylene product chain and glycerin into the propylene chain. Ethanol is too valuable a commodity for the manufacture of plastics, detergents, fibers, films and pharmaceuticals to be used as a motor fuel. Glycerin, a by-product from biodiesel production, will be generated in very large amounts, and it can be used in the propylene chain. Byproducts of agricultural production – bagasse, cane leaf materials, corn stover, rice husks, and poultry and hog wastes – could fulfill some of the energy requirements of the re-engineered plants.

Biomass Feedstock

Raw materials include algae, corn, sugarcane, soybeans or waste biomass like corn stover, bagasse, and municipal solid waste. Algal biomass contains three main components: carbohydrates, proteins and natural oils. Algae contains 2% to 40% of lipids/oils by weight. These components in algae can be used for fuel or chemicals production in three ways, mainly production of methane via biological or thermal gasification, ethanol via fermentation or conversion to esters by transesterification (Sheehan et. al, 1998). Corn led in annual production of grain crops in the U.S. with 330,000 tons per year in 2006 followed by wheat 65,000, sugar beets 30,000, sugar cane 25,000 sorghum 15,000 and oats, 10,000 (Snyder, 2007). The annual production of vegetable oil crops in 2000 in the U.S. was soybeans with 2,770 million bushels, sunflower with 3,580 bushels and cottonseed with 402 million bushels (Paster et al., 2003). In the Gulf coast, sugarcane, rice, soybean, cotton, corn, hay, sorghum, and wheat are grown on ~3.5 MM acres. These crops produce large quantities of agricultural residues such as bagasse, corn stover, and rice husks. Currently, most of these agricultural residues are inefficiently burnt, either in the field or for steam/power generation. A significant number of livestock and poultry producers are seeking treatment alternatives for generated wastes (Perlack, et al., 2005 and de Hoop, 2007).

Biomass Products

Demand for products from biomass will have to come from displacing comparable materials from current processes. A product from a new plant can expect to penetrate no more than 10% of the existing market base on historical experience. Government subsidies and incentives tend to be of limited time and short term value. Projected bulk chemicals from biobased feedstocks are ethanol, butanol and glycerin. Specialty chemicals such as organic acids, including acetic, propionic and butyric acids, have been produced on a pilot scale by anaerobic digestion of pretreated cellulose wastes, and economic evaluations have shown an economic price based on a 15% return on investment to be comparable to the current sales price of the compounds (Granada, 2007). The Department of Energy has identified twelve building block chemicals that can be converted to high value products using biological or chemical conversion of sugar that were screened from 30 chemicals, called top value-added chemicals from biomass (Werpy and Peterson, 2004).

The products include polymers from fatty acid esters, propylene glycol and 1,3-propanediol from glycerin, ethylene and ethylene derivatives from biobased ethanol, acetic acid from anaerobic digestion and also other chemicals derived from the building blocks as shown in Figure 3.

Evaluation Method

The transesterification process flow diagram is developed using Aspen HYSYS 2006® for the production of fatty acid methyl and ethyl esters and glycerol as byproduct. The fatty acid methyl and ethyl esters are used for the manufacture of polyurethane foams. Using Aspen HYSYS 2006®, the glycerol byproduct is converted to propylene glycol. These cases are exported to Aspen Icarus Process Evaluator 2006® and detailed economic estimates of the processes are obtained. The process flow diagrams are then converted to single block diagrams with overall mass and energy balances to be included in the Chemical Complex Analysis System.

The Chemical Complex Analysis System is used to determine the best configuration of plants in a chemical complex based on economic, energy, environmental and sustainable costs. It incorporates a flowsheeting component where simulations of the plants in the complex are entered. Each simulation includes the process or block flow diagram with material and energy balances, rate equations, equilibrium relations and thermodynamic and transport properties for the process units and heat exchanger networks. Multi-criteria optimization is used with Monte

Carlo simulation to determine the optimal configuration of plants in chemical production complex and sensitivity to prices, costs and sustainability credits/costs.

Conclusion

Results from using the System had soybean and algae oil going from the transesterification process into polyurethane foams and propylene glycol. Ethanol from fermentation goes into the ethylene chain to produce polyethylene. Anaerobic digestion provides acetic acid and cellulose acetate. Gasification, pyrolysis and Fishcher Tropsch synthesis were not in the configuration of plants in the optimal structure. More information and a detailed white paper on this research is available at www.mpri.lsu.edu/Integrating_Biomass_Feedstocks_into_Chemical_Production_Complexes_-_a_White_Paper.pdf.

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