

Minerals Processing Research Institute
Louisiana State University

White Paper

on

Integrating Biomass Feedstocks into Chemical Production
Complexes using New and Existing Processes

by

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November 3, 2008

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Table of Contents

Abstract.....	3
Introduction.....	4
A Research Vision	5
New Frontiers.....	5
The Chemical and Petroleum Refining Industry in the Lower Mississippi River Corridor	6
Development of New Industries based on Renewable Resources that Initially Require Nonrenewable Resources Supplements	9
New Processes for the Chemical Complex - Chemicals from Biomass based Feedstocks	14
Biomass Fermentation	17
The Calvin-Benson Cycle	18
The C4 cycle	19
The CAM cycle.....	19
Biomass Classification and Composition	20
Starch	20
Lignocellulosic Biomass.....	20
Cellulose	21
Hemicellulose	21
Lignin.....	24
Lipids, Fats and Oils	24
Feedstock Availability	25
Biomass availability in United States	25
Biomass availability in Louisiana.....	29
New Feedstock Options – Algae.....	31
Biomass Conversion Routes	36
Biomass Pretreatment	36
Hot Wash Pretreatment.....	37
Acid Hydrolysis	37
Enzymatic Hydrolysis.....	38
Ammonia Fiber Explosion.....	38
Fermentation	38
Anaerobic Digestion	39
Transesterification.....	43
Gasification/Pyrolysis	51
Biomass Conversion Products – by Carbon Number	54

Single-Carbon Compounds.....	54
Methane.....	54
Methanol.....	55
Two-Carbon Compounds.....	55
Ethanol.....	55
Economies of Scale.....	64
Plant Size and Collection Distance.....	64
Corn Stover Cost.....	66
Total Cost of Ethanol as a Function of Plant Size.....	67
Ethanol from Glycerol.....	67
Ethanol from Synthesis Gas Fermentation.....	68
Acetic Acid.....	70
Ethylene.....	71
Three-Carbon Compounds.....	73
Glycerol.....	73
Lactic acid.....	74
Propylene Glycol.....	74
1,3-Propanediol.....	75
Four-Carbon Compounds.....	76
Butanol.....	76
Succinic Acid.....	77
Aspartic acid.....	78
Five-Carbon Compounds.....	78
Levulinic Acid.....	78
Xylitol/Arabinitol.....	80
Itaconic Acid.....	81
Six-Carbon Compounds.....	82
Sorbitol.....	82
2,5-Furandicarboxylic Acid.....	82
Cellulose Acetate.....	83
Vegetable Oil Based Chemicals.....	84
Incorporating Processes for Chemicals from Biomass in Chemical Production Complexes.....	85
Chemical Complex Analysis System.....	96
References.....	97

Abstract

The vision is the development of new industries in the region that are based on renewable resources which supply the products and services of the current industries. Vision includes transitioning existing plants to ones using biomass feedstocks that require nonrenewable resource supplements. The chemical complexes in the Gulf Coast are uniquely positioned to take advantage of bio-derived feedstocks. There is strong agricultural industry in the region, and the Mississippi River provides deep-water ports to ensure continuous supply of bio-feedstocks throughout the year.

Using the Chemical Complex Analysis System, the initial evaluation is for the introduction of plants producing ethanol to go into ethylene product chain and plants using glycerin to go into the propylene chain. This evaluation is including algae which have the potential for being an important source of oil and carbohydrates for chemicals with yields of 15,000 gallons/acre of oil per year.

The analysis will be extended to plants that use biomass contain cellulose, hemicellulose, lignin, fats and lipids and proteins. For biomass containing mainly cellulose, hemicellulose and lignin, plants will employ various pretreatment procedures to separate the components. Steam hydrolysis breaks some of the bonds in cellulose, hemicellulose and lignin. Acid hydrolysis solubilizes the hemicellulose by depolymerizing hemicellulose to 5-carbon sugars such as pentose, xylose, and arabinose. Green US chemical plants will incorporate separations processes for extracting the chemicals from 5-carbon sugars. The cellulose and lignin stream is then subjected to enzymatic hydrolysis where cellulose is depolymerized to 6-carbon glucose and other 6-carbon polymers which separate the cellulose stream from lignin. Three separate streams are obtained from biomass. Plants will be included to have the cellulose and hemicellulose monomers, glucose and pentose undergo fermentation to yield chemicals like ethanol, succinic acid, butanol, xylitol, arabinitol, itaconic acid and sorbitol. The lignin stream is rich in phenolic compounds which can be extracted in a plant, and the stream can be dried to form char and used in a plant for gasification to produce syngas. A plant for pyrolysis or thermal decomposition of biomass generates a complex liquid mixture and a solid similar to powdered coal. The liquid can be used to manufacture phenol-formaldehyde resins. A plant for direct chemical conversion of biomass, such as hydrogenation of lignin will yield phenols, and synthesis gas can be fermented to ethanol.

Plants with biomass feeds containing oils, lipids and fats can be transesterified to produce fatty acid methyl and ethyl esters and glycerol. The glycerol from transesterification can be converted to propylene glycol, 1, 3-propanediol and other compounds in plants that can replace ones using natural-gas-based chemicals. Plants using vegetable oils, particularly soybean oil, as feedstock will be evaluated for the production of various polyols with a potential to replace propylene oxide based chemicals. The acrylated epoxidized triglycerides from soy bean oil can be used as alternative plasticizers in polyvinyl chloride as a replacement for phthalates. Vegetable oils can be directly blended in petroleum diesel fractions, and catalytic cracking of these fractions produce biomass-derived fuels for chemicals.

Incorporating processes using biomass as feedstocks in the chemical production complex of existing plants gives a superstructure of plants that can be used to determine the optimal configuration of plants. The objective function used for the optimization is the triple bottom line that incorporates economic, environmental and sustainable costs. Triple bottom line costs are being evaluated and include economic and environmental costs and sustainable credits and costs. These are to be used in the multicriteria, mixed-integer nonlinear programming problem which will use global and local solvers to determine the Pareto optimal solutions. Monte Carlo Analysis is to be used to determine sensitivity of the optimal solution to the parameters in the optimization problem.

Consideration for extensions of the base case include plants in the Gulf Coast Region (Texas, Louisiana, Mississippi, Alabama) and demonstration that the methodology can be applied to other chemical complexes of the world.

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. The chemical production complex in the lower Mississippi River corridor is used to demonstrate the integration of these new plants into an existing infrastructure. Potentially new processes are evaluated based on proposed selection criteria, and simulations of these processes are performed using HYSYS (Indala, 2004). Then the optimal configuration of new and existing plants is determined by optimizing the triple bottom line based on economic, environmental, and sustainable costs using the Chemical Complex Analysis System (Xu, 2004).

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 sustainability requirements. The optimal configuration of plants in a chemical production 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 in Jurong Island (Singapore), and Equate (Kuwait), among others (Xu, 2004).

A Research Vision

The research vision is to lead in the development of new industries in the region that are based on renewable resources which supply the needed goods and services of the current ones. The vision includes converting existing plants to ones that are based on renewable resources requiring nonrenewable resource supplements.

An example is ethanol produced from corn that was grown with chemical fertilizers produced from fossil fuels. Ethanol reduces greenhouse gas emissions by 22% compared to gasoline (Bourne, 2007). Another is a wind farm of turbines producing electricity where the turbines were built with materials that required energy from fossil fuels. Wind is considered the greatest source of renewable energy, and 10,000 MW (megawatts) have been installed in the U. S. selling for 4-7 cents per kWh, the least expensive source of energy.

This vision is an essential component of sustainable development. It embodies the concepts that sustainability is a path of continuous improvement, wherein the products and services required by society are delivered with progressively less negative impact upon the Earth. It is consistent with the Brundtland Commission report that defines the term as development which meets the needs of the present without sacrificing the ability of the future to meet its needs (United Nations, 1987).

New Frontiers

The Gulf Coast region is in a transition not ever experienced in the nation's history. Losses from natural disasters, plants relocating to other parts of the world, environmental deterioration and competition from imports require a new vision and direction. This research is driven by a desire to understand how sustainable industries can evolve from ones based on non-renewal resources. Chemical plants in the Gulf Coast that rely exclusively on natural gas as a feedstock face closure. To remain operational many of these plants must carefully evaluate migration to new feedstocks. The Gulf Coast is uniquely positioned to take advantage of bio-derived feedstocks. There is strong agricultural industry in the region, and the Mississippi River provides deep-water ports to ensure continuous supply of bio-feedstocks throughout the year.

Existing natural-gas-intensive processes, such as agricultural chemical production, can be reconfigured as bio-derived chemical plants. For example, the Farmland Industries ammonia plant in Pineville, Louisiana has recently migrated from ammonia production to bio-diesel production from soybean oil. Farmland Industries is one of the 14 companies that have closed 17 ammonia plants with a total capacity of 5.6 million tons per year (Byers, 2006).

The Pineville example is both encouraging and discouraging for the Gulf Coast. The Pineville bio-diesel facility is in operation but with substantially fewer employees, about 20 employees now compared to over 100 as a fertilizer plant. It is anticipated new employees will be hired as the facility moves from 100,000 to 200,000 gallons of bio-diesel fuel per year. This is somewhat encouraging, but there is a net loss in jobs.

What is most disturbing for the region is the ultimate use of the remaining sections of the ammonia plant in Pineville. The new bio-diesel plant was constructed by modifying the existing water treatment facility in the ammonia plant with some improvements to the control room. However, the majority of the plant, its reactors, separators, distillation columns, etc. have been sold to China. This Louisiana facility is being disassembled piece by piece and being moved to mainland China where it will be used once again to produce ammonia.

The opportunity existed for this plant to be reconfigured to make value-added chemicals here in the United States, but this alternative was not considered. This research will evaluate potential alternatives, including the expertise to help evaluate ethanol and bio-diesel as feedstocks to existing chemical plants. However, the profitability of these migrated plants is inextricably linked to energy efficiency. Processing bio-derived chemicals requires large steam and electrical demands which must be met through cogeneration and on-line optimization. There is virtually no chance for profitable operation if these plants rely on utility.

Our food security is moving into the hands of major agricultural chemicals exporting countries such as Saudi Arabia, Russia, the Ukraine and Venezuela as high natural gas prices result in the outsourcing of the U. S. agricultural chemical industry, at least ammonia. About 40% of U. S. food production is credited to commercial fertilizers. Natural gas, the raw material for the production of nitrogen fertilizer, is 93% of the cost of production (Wilson, 2006). Also, imported phosphate from Morocco is required to supplement a diminishing domestic supply (Hertwig, 2006). Mosaic, Incorporated has announced intent to produce ammonia from petroleum coke that is available from processing heavy crude oil from Venezuela (Thrasher, 2006).

The Chemical and Petroleum Refining Industry in the Lower Mississippi River Corridor

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). Louisiana's chemical industry is the largest single employer with nearly 26,000 direct employees, a number that does not include the thousands of contract and maintenance employees that work at the plants year round. These jobs generate \$5.9 billion in earnings and \$125 million in state and local taxes on personal income. Over a billion dollars is spent in Louisiana annually with Louisiana suppliers according to the Louisiana Chemical Association (www.lca.org).

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 carbon nanotubes and energy integration. It will provide a basis for research on converting processes based on nonrenewable resources to ones based on renewable resources.

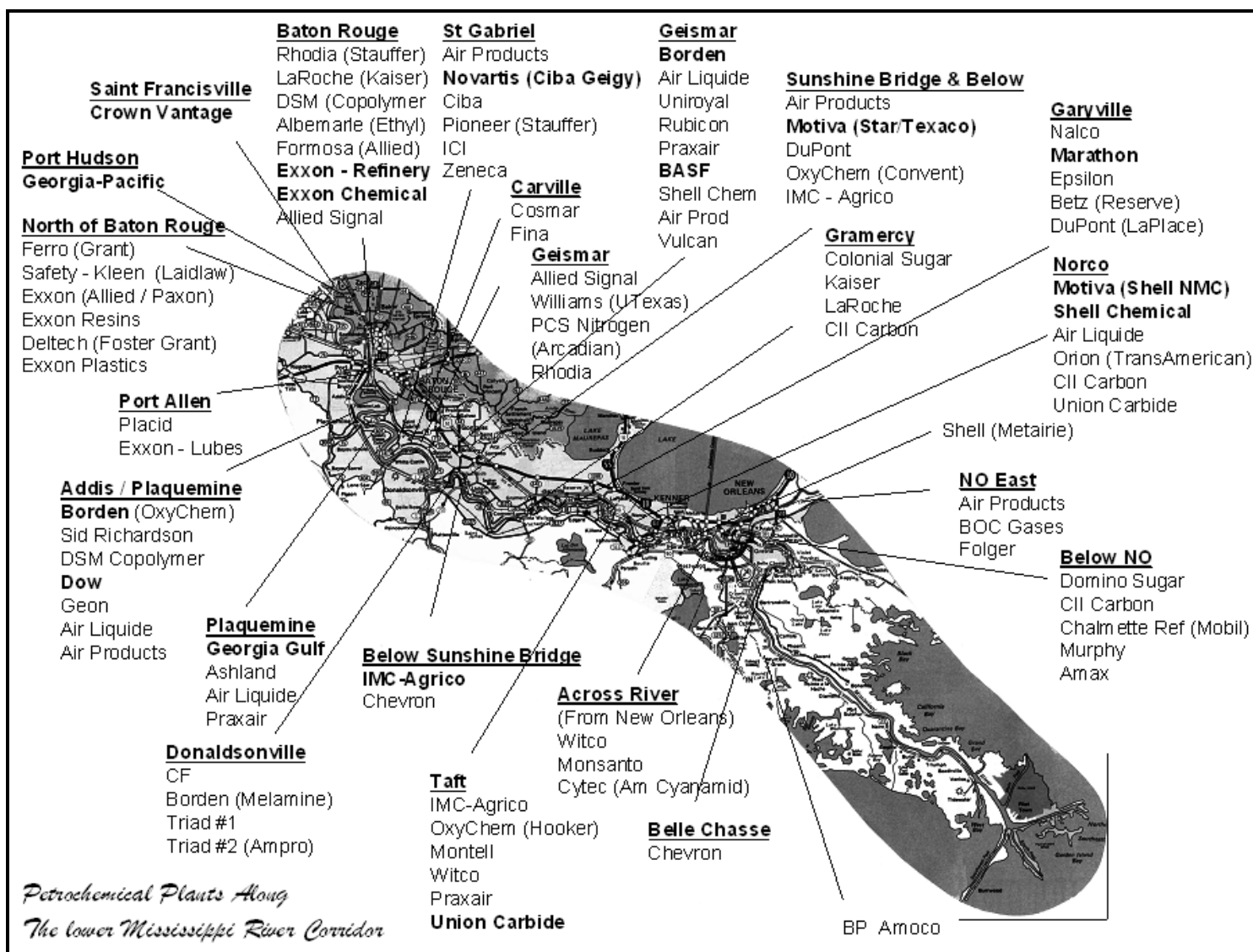


Figure 1. Plants in the Lower Mississippi River Corridor, from Peterson, 2000.

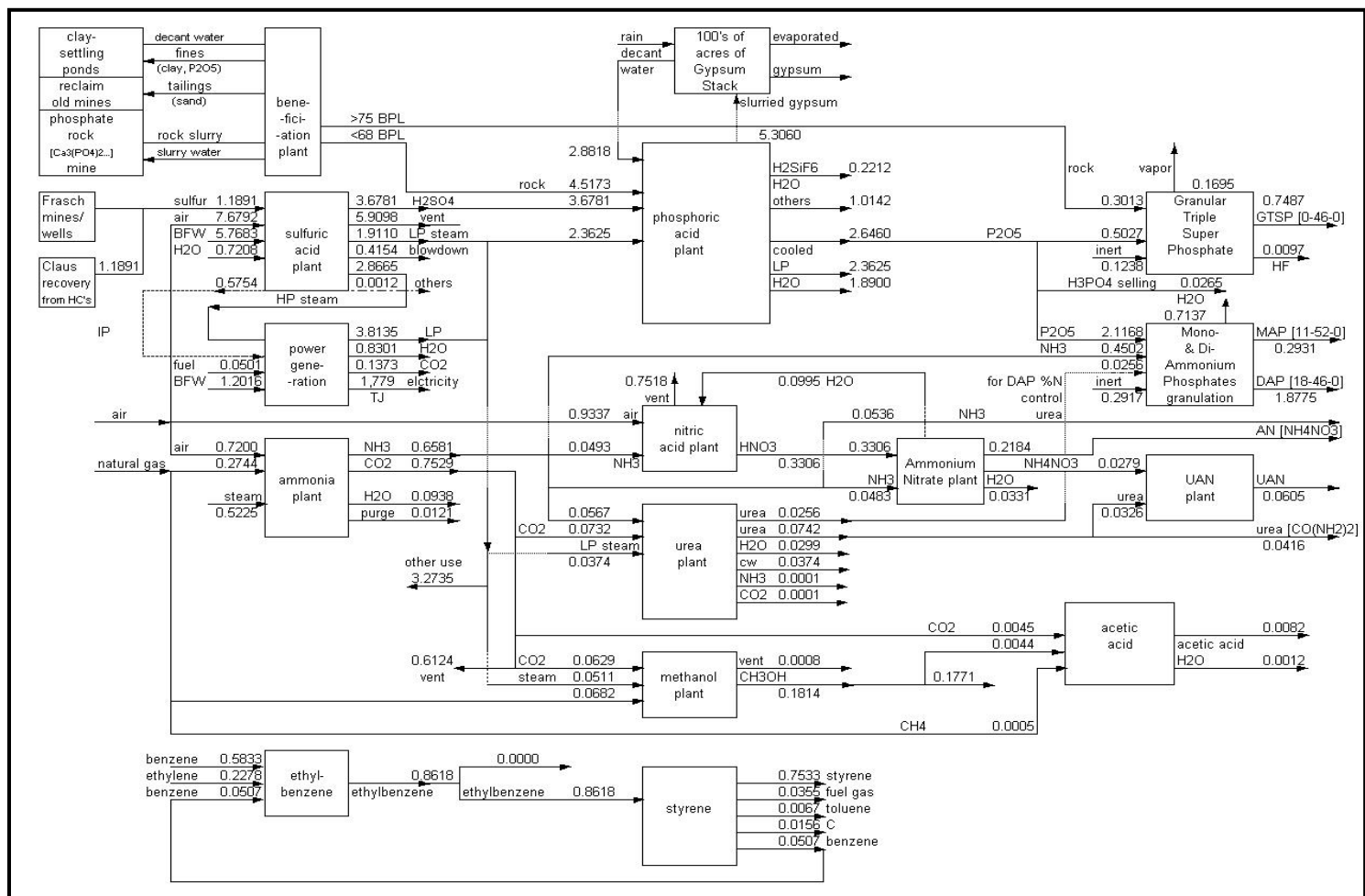


Figure 2. Chemical Production Complex in the Lower Mississippi River Corridor, Base Case, Flow Rates - Million Metric Tons per Year from Xu, 2004

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.

The raw materials used in the base case of the chemical production complex in Figure 2 include air, water, natural gas, sulfur, phosphate rock, ethylene and benzene as shown on Figure 2. The products are mono- and di-ammonium phosphate (MAP and DAP)-, urea, ammonium nitrate, and urea ammonium nitrate solution (UAN), phosphoric acid, ammonia, methanol, acetic acid, ethylbenzene and styrene. The flow rates shown on the diagram are in million metric tons per year. Intermediates are sulfuric acid, phosphoric acid, ammonia, nitric acid, urea, carbon dioxide and ethylbenzene. The intermediates are used to produce MAP and DAP, GTSP, urea, ammonium nitrate, acetic acid, UAN, and styrene. Ammonia is directly applied to crops and as a synthetic intermediate. MAP, DAP, UAN and GTSP are directly applied to crops. Phosphoric acid can be used in other industrial applications. Methanol is used to produce formaldehyde, methyl esters, amines and solvents along with many other organics, and is produced using ammonia plant byproduct - carbon dioxide. Acetic acid, ethyl benzene and styrene are used as feedstocks in other chemical processes. Emissions from the chemical production complex include sulfur dioxide, nitrogen oxides, ammonia, methanol, silicon tetra fluoride, hydrogen fluoride and gypsum.

Development of New Industries based on Renewable Resources that Initially Require Nonrenewable Resources Supplements.

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.

An initial evaluation of various biomass feedstock based processes is shown in Figure 3. This shows raw materials including starch, sugars, cellulose and natural oils converted using processes like transesterification, fermentation and anaerobic digestion to products like ethanol, fatty acid esters and acetic acid.

Ethanol is readily converted to ethylene in a process that uses an activated alumina catalyst in a fluidized bed at 300°C with a 99% conversion (Wells, 1999). There are five companies operating more than a dozen ethylene plants in the chemical production complex in the lower Mississippi River corridor (Peterson, 2000). These plants produce about 1.0 million pounds per

year of ethylene from natural gas and naphtha. In this complex there are about 150 chemical plants producing a wide range of petrochemical that are used in housing, automobiles, fertilizer and numerous other consumer products that use 1.0 quad (10^{15} BTUs per year) of energy (Peterson, 2000).

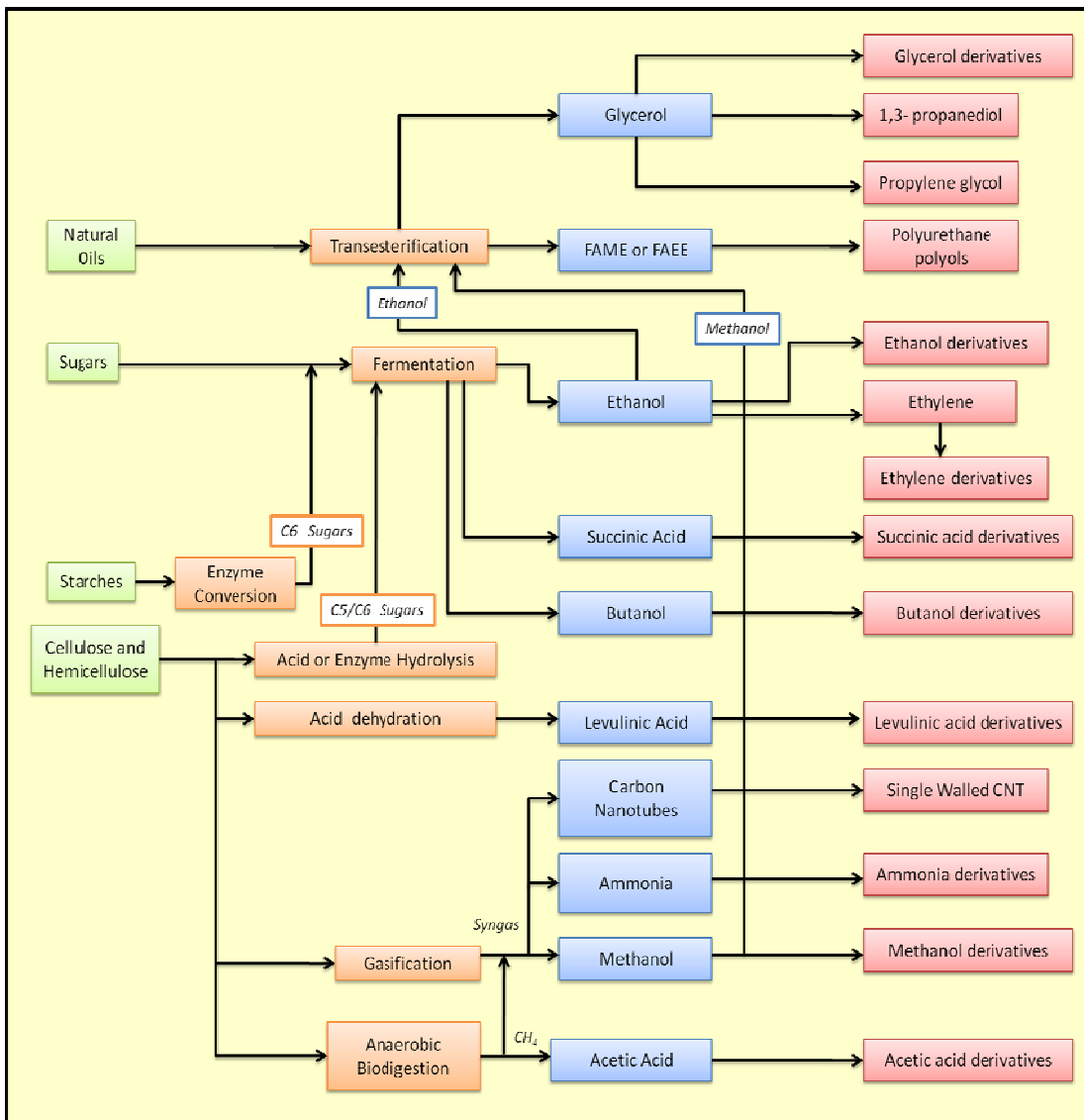


Figure 3. Biomass feedstock based processes for the production of chemicals.

Dow Chemical and Crystalsev, a Brazilian sugar and ethanol producer, plan to build a 300,000 m.t./yr ethylene plant in Brazil to manufacture 350,000 m.t./yr of low density polyethylene from ethanol. Braskem, a Brazilian petrochemical company, plans to produce 200,000 m.t./yr of high density polyethylene from sugar (C&E News, 2007b). Also, Solvay's South American affiliate plans to build a plant in Santo Andre, Brazil, to produce 60,000 tons per year of sugar cane derived ethylene which will be combined with chlorine to produce poly vinyl chloride plastic (PVC) (C&E News, 2007c).

Sustainable chemical processes based on renewable resources require the availability of raw materials for biobased feedstocks, demand for products from these feedstocks and capacities of plants that produce these materials. In converting existing chemical plants to ones using renewable resources, there will be a transition where nonrenewable resource supplements will be required. All of the chemicals from biomass, e. g., ethanol, glycerin, xylitol, synthesis gas, are intermediates for final products in the marketplace, e.g., vehicles, building materials, household products. The converted and new plants will be part of the infrastructure provided in chemical production complexes to use existing transportation, utilities, maintenance services, raw materials suppliers and product end users.

Thousands of different industrial bioproducts are produced today, and they can be categorized into four major areas. One is sugar and starch bioproducts obtained through fermentation and chemical processes and include alcohols, acids, starch and xanthium gum derived from feedstocks including corn, sugarcane, sugar beets, rice, potatoes, sorghum grain and wood. Another is oil and lipid-based bioproducts obtained through chemical processes and include fatty acids, oils alkyd resins and glycerin derived from feedstocks including soybeans, rapeseed and other oilseeds. A third is gum and wood chemicals including tall oil, alkyd resins, rosins, pitch, fatty acids and turpentine derived from trees. The fourth is cellulose derivatives and plastics including cellulose acetate (cellophane) and triacetate, cellulose nitrate, alkali cellulose and regenerated cellulose derived from wood pulp and cotton linters. A fifth category would include industrial enzymes used for biocatalysts in the production of starch, sugar alcohols and oils. They are used in detergents, tanning and textile sizing (Pastor, et al., 2003). The corn product chain given in Figure 4 shows the bioproducts from corn. This work acknowledges these industries, but is concerned with new processes that use biomass as a feedstock for chemicals. Processes that can be considered as not contributing additional carbon dioxide to the atmosphere are evaluated for inclusion in the chemical production complex.

Chemicals from biobased feedstocks are produced by biochemical processes including fermentation (bacterial and fungal) and anaerobic digestion and by chemical processes including gasification, pyrolysis, transesterification, hydrogenation and hydrocracking. Descriptions of biochemical processes are given by Klass, 1998 for existing industries and by Paster et al., 2003 for existing industries and potential processes using biomass. Top value-added chemicals from biomass have been analyzed by Werpy and Peterson, 2004. Descriptions of chemical processes are given by Klass, 1998 for existing industries and by Spath and Dayton, 2003 for existing industries and potential processes.

Biobased feedstocks come from virgin biomass and waste biomass. Virgin biomass includes corn and soybean oil, for example, and waste biomass includes agricultural residues e.g., bagasse from sugar cane, wood residues, sawdust, and animal waste. The unit costs of the biobased feedstocks are set by their alternate uses. For virgin biomass, typically a food or animal feed, this use sets the cost. For waste biomass, these materials are typically used as a fuel, and their cost would be equal to the fuel replacement cost. These feedstocks can be classified in other ways as given by Cockrem, 2007:

- Substrate: oil based (fatty acids, glycerol) and carbohydrate based (corn)
- Fermentation Feedstock: Contain significant solids (milled corn) and clear liquid (liquefied starch or sugars, cane juice)
- Seasonality and Storage Stability: Reasonably stable (oilseeds, corn), Must be used fresh (sugar cane) and degrades slowly (corn stover, crop residue wood, grasses)

Details for biomass availability and use in the United States are given by Perlack, et al., 2005 and in the Gulf coast by de Hoop, 2007. It has been estimated that agricultural lands in the United States can provide about 1.0 billion dry tons of sustainable, collectable biomass and continue to meet food, feed and export demands. The distribution in million dry tons is: 87 from grains, 377 from perennial crops, 446 from crop residue and 87 from animal manures and other sources. Forest lands can provide an additional 370 million dry tons of biomass annually.

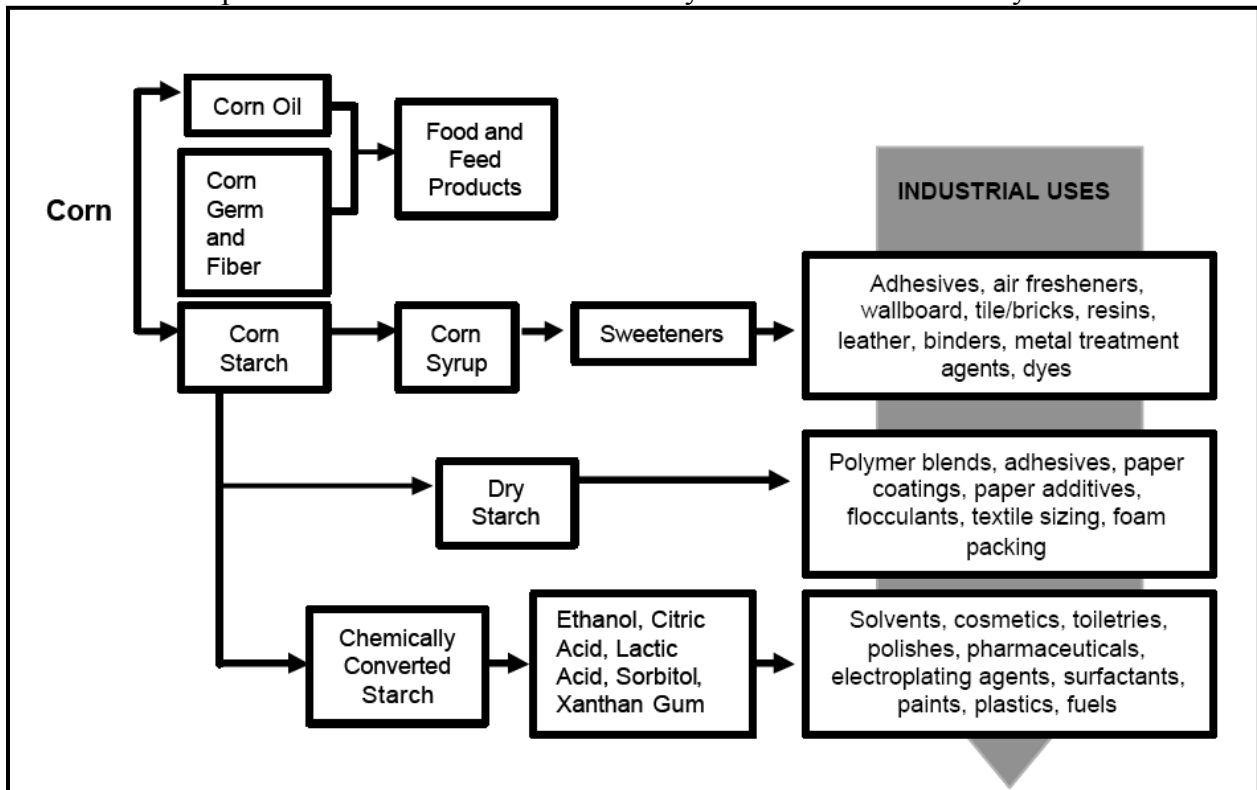


Figure 4 Bioproducts from Corn, the Corn Product Chain, from Paster, et al., 2003

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).

The Gulf coast is one of the leading producers of sugarcane in the U.S.A with approximately 2.0 billion pounds of raw sugar produced in 2005 (LSU Agricultural Center, 2007). This high volume of sugar production also produces waste products like molasses and bagasse. Approximately, 122,000 wet tons of bagasse is produced by the sugar industry. Currently, bagasse is used as boiler fuel in place of natural gas. Bagasse has high water content, and this water causes a decrease in boiler efficiency. For dry bagasse, the boiler efficiency for bagasse combustion is around 80% whereas the efficiency reduces to 51% for a moisture content of 60% (Klass, 1998). Dewatering and drying methods for the bagasse are possible to increase the efficiency, but they require energy from fossil fuels at an additional cost. The cost of fossil fuels for drying biomass has a diminishing effect on boiler efficiency. As a result, alternate routes to convert the bagasse to useful chemicals such as ethanol, succinic acid and fumaric acid that have a high market value than fuel. Water content is not a factor in microbial processes where cellulosic biomass is decomposed into glucose.

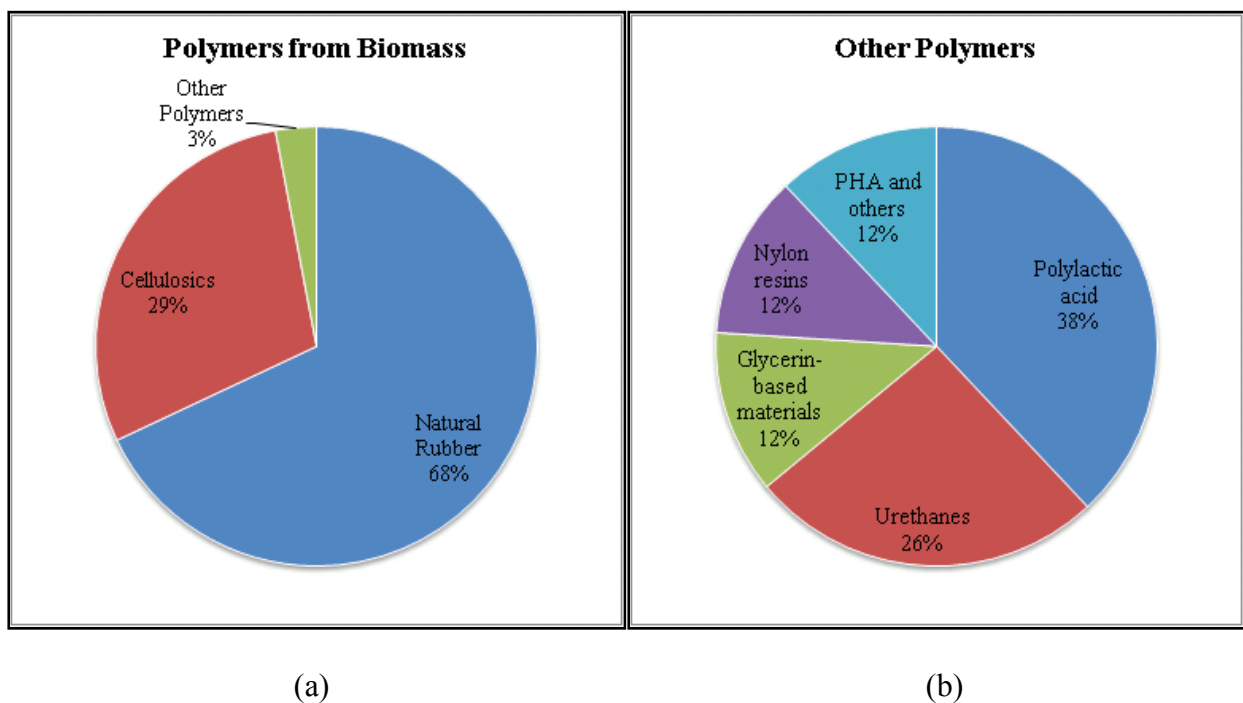


Figure 5 (a) 2007 Production of polymers from biomass (13,000 million metric tons) and (b) breakdown of other polymers (Tullo, 2008).

Demand for products from biomass will have to come from displacing comparable materials from current processes. 13,000 million metric tons of polymers was made from biomass in 2007 as shown in Figure 5(a) out of which 68% is natural rubber. Figure 5(b) shows the division of new polymers from biomass, which attributes to a total of 3% of the present market share of biobased polymers. A product from a new chemical plant can expect to penetrate no more than 10% of the existing market based on historical experience. However, once the benefits of a new product is established, for example replacing glass in soda bottles with

petrochemical based polyethylene terephthalate, the growth is rapid over short period of time (Tullo, 2008). Most renewable processes for making polymers have an inflection point at \$70 per barrel of oil, above which, the petroleum based process costs more than the renewable process. For example, above \$80 per barrel of oil, polylactic acid (PLA) is cheaper than polyethylene terephthalate (PET). The Table 1 gives a list of companies that have planned new chemical production based on biomass feedstock along with capacity and projected startup date. 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).

A number of specialty chemical companies have announced plans to make commodity and specialty chemicals (Tullo, 2007a). Huntsman Corporation will produce propylene glycol from glycerin made as a co-product from biodiesel. Dow and Solvay are planning to manufacture epoxy resin raw material epichlorohydrin from a glycerin-based route to propylene glycol. Rohm and Haas is exploring high-energy crops for cellulosic ethanol to produce methacrylate monomers for applications in paints and acrylic sheets. DuPont and Tate & Lyle Bio Products have started-up a 100 million pounds per year propanediol plant using corn sugar as the feedstock in Loudon, TN which will be used to produce DuPont's Sorona polymer (CEP, 2007). Celunol is operating the first U. S. cellulosic ethanol pilot plant in Jennings, LA using bagasse and is completing a 1.4 million gallon per year demonstration facility. Celunol's technology has been licensed to Marubeni Corporation (Tokyo, Japan) which operates a 1.4 million litres per year cellulosic ethanol plant using wood waste (McCoy, 2007).

New Processes for the Chemical Complex - Chemicals from Biomass based Feedstocks

The following discussion reviews the numerous potential processes that can use biomass as a feedstock for chemicals manufacture based on availability of raw materials, demand for products and capacities of process units. In Figure 6, the routes for the use of biological materials are outlined to produce chemicals and fuels. These include transesterification of vegetable oils, fermentation of starch and cellulose, anaerobic digestion of cellulose, gasification, pyrolysis, hydrogenation and hydrocracking. Transesterification of vegetable oils produces fatty acid methyl and ethyl esters (FAME and FAEE), predominately palmitic, oleic and linoleic from soybean oil (Marchetti, et al., 2007). Fermentation of starch produces ethanol and other alcohols. Anaerobic digestion of cellulose produces acetone and higher ketones. Gasification or partial combustion of biofeedstocks produces synthesis gas or "syngas", a mixture of mainly carbon monoxide and hydrogen that is a starting material for the manufacture of ammonia, methanol, urea and a number of other important chemicals (Xu, 2004). Pyrolysis or thermal decomposition generates a complex liquid mixture and a solid similar to powdered coal. The liquid can be used to manufacture phenol-formaldehyde resins, Paster, et al., 2003. The diagram

Table 1 Biomass based chemical production companies.

Company Name	Location	Startup Date	Product	Capacity (m.t. per year)	Notes
Telles	Clinton, Iowa	Q2, 2009	Polyhydroxy alkanate (PHA) or Mirel	50,000	Joint venture between Metabolix and Archer Daniels Midland, facility will house fermenters full of K-12 strain of <i>Escherichia coli</i> genetically modified to produce PHA directly. Process advantages include lower energy consumption (about 3.5% of that required for conventional plastics) and biodegradability of PHA.
Cereplast	Seymour, Indiana	Completed, 2008	polylactic acid (PLA) based compound	25,000	Cereplast works with PLA from NatureWorks to make it more heat resistant and comparable to polypropylene or polystyrene.
PSM North America	China	In Production	Plastarch Material (PSM)	100,000	Plastarch is a resin comprised of 80% industrial starch and 8% cellulose mixed with sodium stearate, oleic acid and other ingredients. It can be processed like a petrochemical plastic, can withstand moisture and is heat tolerant.
Synbra	The Netherlands	2009	polylactic acid (PLA)	5,000	PLA technology developed by Dutch lactic acid maker Purac and Swiss process engineering firm, Sulzer.
Green Bioscience	Tianjin, China	-	Polyhydroxy alkanate (PHA)	10,000	DSM has invested in this firm.

in Figure 6 does not include the direct chemical conversion of biomass, such as hydrogenation of lignin to phenols (Klass, 1998) and fermentation of synthesis gas to ethanol (Snyder, 2007). The following sections describe the state of development and technology for new processes to convert biomass feedstocks to chemicals.

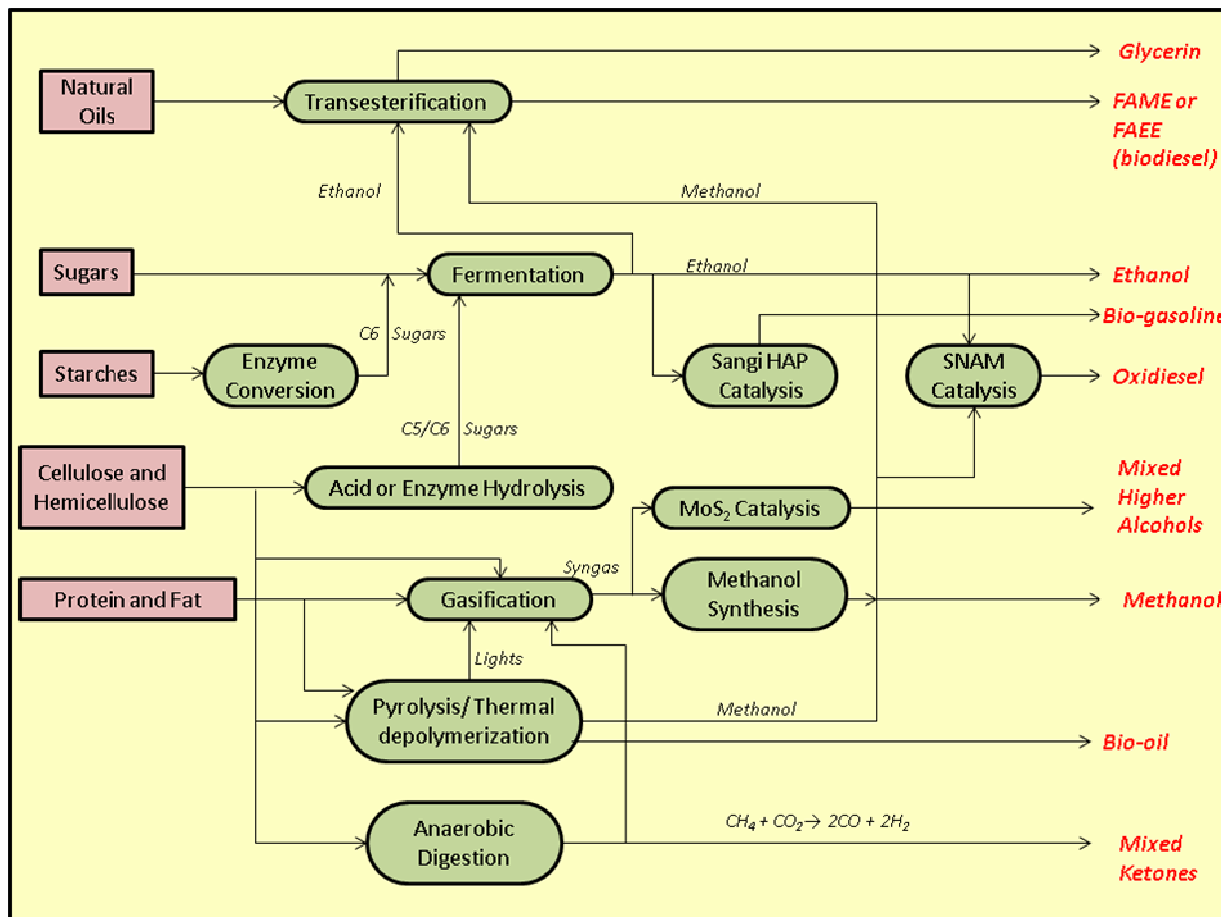


Figure 6 Conversion Routes of Biomass Feedstock to Chemicals

An economic evaluation was made by Wright and Brown, 2007 for five plants each having a capacity of 150 million gallons of gasoline equivalent per year producing the following products: grain ethanol, cellulosic ethanol, methanol hydrogen and Fischer-Tropsch liquids. Raw material cost was \$2.12 per bushel for corn for grain ethanol and \$50 per mega gram (ton) for cellulosic feedstock. Capital and operating cost were based on 2005. The results are given in Table 2. They concluded that advanced biofuels plants have a capital cost of the order at five times that of a comparable sized starch ethanol plant based technology. The ranking for capital and operating cost are the same with hydrogen, being the least expensive followed by methanol, cellulosic ethanol and Fischer-Tropsch liquids. It was concluded that neither biochemical nor thermochemical have a clear advantage in capital or operating costs for the production of advanced biofuels.

Table 2 Capital and Operating Costs for a 150 MMGPY Gasoline Equivalent Plant (2005 dollars) from Wright and Brown, 2007

Capital Cost Plant Type	Total Capital Cost (\$ million)	Capital Cost per unit of Production (pbpd*)	Operating Cost (\$ per gallon)**
Grain Ethanol	111	13,000	1.22
Cellulosic Ethanol	756	76,000	1.76
Methanol	606	66,000	1.28
Hydrogen	543	59,000	1.05
Fischer-Tropsch Liquids	854	86,000	1.80

* per BPD gasoline equivalent

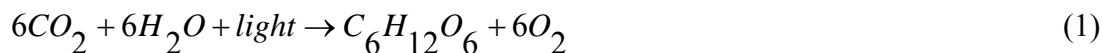
** gallons of gasoline equivalent

Biomass Fermentation

The world has a wide variety of bio feedstocks that can be used for the production of chemicals. Biomass includes plant materials such as trees, grasses, agricultural crops, and animal manure. The components of biomass are shown in Figure 7. Biomass can be divided into five categories as shown in the figure: starch, cellulose, hemicellulose lignin and oils. Cellulose hemicellulose and lignin are components of woody biomass, grasses, stalks, stover etc. Starch and cellulose are both polymeric forms of hexose, a 6-carbon sugar. Hemicellulose is a polymer of pentose. Lignin is composed of phenolic polymers, and oils are triglycerides. Other biomass components, which are generally present in minor amounts, include sterols, alkaloids, resins, terpenes, terpenoids and waxes. In Figure 8 photographs are given of some of these biomass feedstocks to show the form of the raw materials that are used to produce sugar and oil.

Different mechanisms of photosynthesis for biomass give different compositions and abundance which determine feedstock availability in United States and in the Gulf Coast. Biomass feedstocks can be compiled based on carbon number in the chemicals that use biomass feedstock and conversion routes. Some of these chemicals are presently made from non-renewable feedstock like natural gas and petroleum while others are new chemicals that have potential to replace non-renewable feedstock based chemicals. This description is not exhaustive but serves as a starting point for identifying the processes and feedstocks for conversion to chemicals.

Biomass is the photosynthetic sink by which atmospheric carbon dioxide and solar energy is fixed into plants (Klass, 1998). These plants can be used to produce the stored energy in form of fuels and chemicals. The primary equation of photosynthesis is given by Equation 1.



The photosynthesis process utilizes inorganic material (carbon dioxide and water) to form organic compounds (hexose) and releases oxygen. The Gibbs free energy change for the process is +470 KJ per mole of CO₂ assimilated, and the corresponding enthalpy change is +470 KJ. The positive sign on the energy denotes that energy is absorbed in the process. Photosynthesis is a two phase process comprising of the “light reactions” (in the presence of light) and “dark reactions” (in the absence of light).

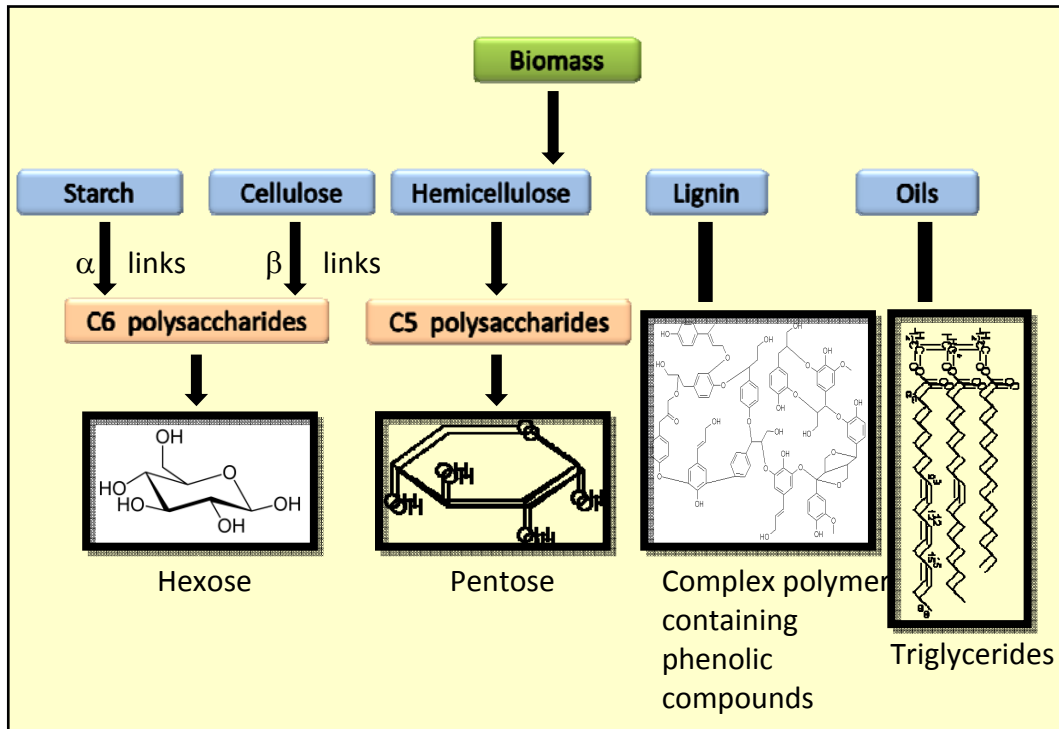


Figure 7 Components of Biomass

The light reactions are common to all plant types, where eight photons per molecule of carbon dioxide excite chlorophyll to generate ATP (adenosine triphosphate) and NADPH₂ (reduced nicotinamide adenosine dinucleotide phosphate) along with oxygen (Klass, 1998). The ATP and NADPH₂ react in the dark to reduce CO₂ and form the organic components in biomass via the dark reactions and regenerate ADP (adenosine diphosphate) and NADP (nicotinamide adenosine dinucleotide phosphate) for the light reactions.

The dark reactions can proceed in accordance with at least three different pathways listed below:

The Calvin-Benson Cycle: Plant biomass species which use the Calvin Benson cycle to form products are called the C3 plants (Klass, 1998). This cycle produces the 3-carbon intermediate 3-phosphoglyceric acid and is common to fruits, legumes, grains and vegetables. C3 plants usually exhibit low rates of photosynthesis at light saturation, low light saturation points, sensitivity to oxygen concentration, rapid photorespiration and high CO₂ compensation points. The CO₂ compensation point is the CO₂ concentration in the surrounding environment below which more CO₂ is respired by the plant than is photosynthetically fixed. Typical C3 biomass species are alfalfa, barley, Chlorella, cotton, Eucalyptus, Euphorbia lathyris, oats, peas, potato,

rice, soybean, spinach, sugar beet, sunflower, tall fescue, tobacco and wheat. These plants grow favorably in cooler climates.

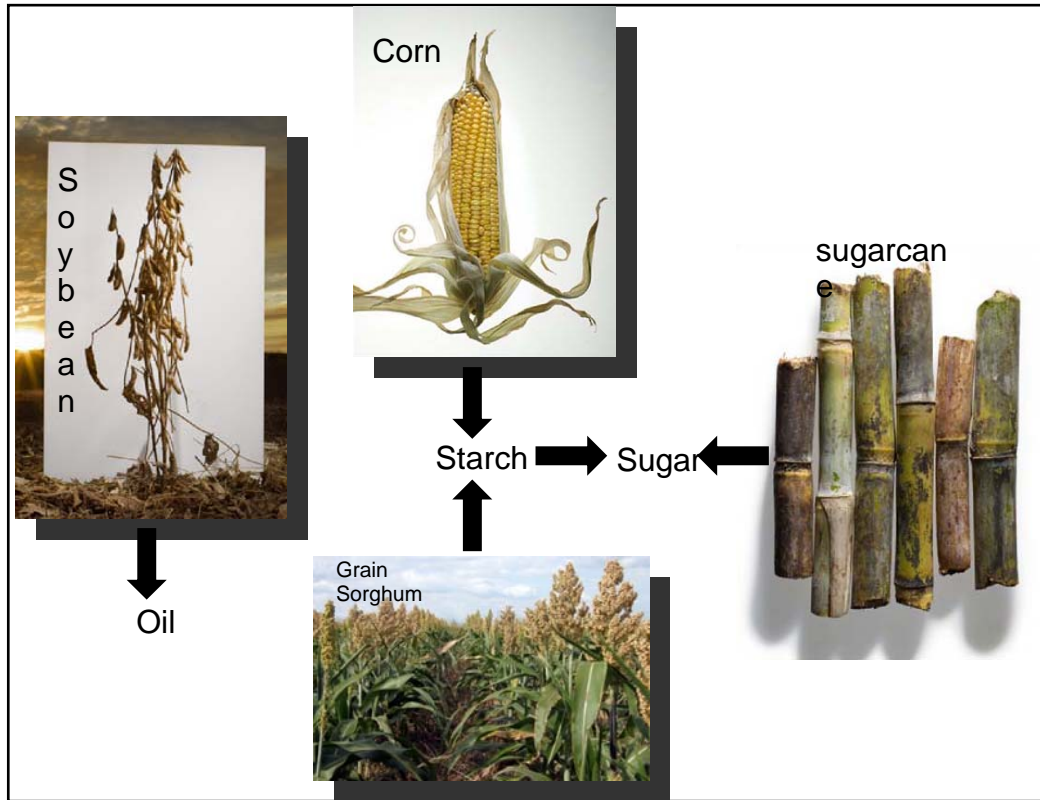


Figure 8 Photographs of Biomass Raw Materials (Source Bourne, 2007)

The C4 cycle: In this cycle, CO₂ is initially converted to four-carbon dicarboxylic acids (malic or aspartic acids) (Klass, 1998). The C4 acid is transported to bundle sheath cells where decarboxylation occurs to regenerate pyruvic acid, which is returned to the mesophyll cells to initiate another cycle. The CO₂ liberated in the bundle sheath cells enter the C3 cycle described above and it is in this C3 cycle where the CO₂ fixation occurs. The subtle difference between the C3 and C4 cycles are believed to be responsible for the wide variations in biomass properties. C4 biomass is produced in higher yields with higher rates of photosynthesis, high light saturation points, low levels of respiration, low carbon dioxide compensation points and greater efficiency of water usage. Typical C4 biomass includes crops such as sugarcane, corn, sorghum and tropical grasses like Bermuda grass.

The CAM cycle: The CAM cycle is the Crassulacean Acid Metabolism cycle, which refers to the capacity of chloroplast containing biomass tissues to fix CO₂ via phosphoenolpyruvate carboxylase in dark reactions leading to synthesis of free malic acid (Klass, 1998). The mechanism involves b-carboxylation of phosphoenolpyruvic acid by this enzyme and the subsequent reduction of oxaloacetic acid by maleate dehydrogenase. Biomass species in the CAM category are typically adapted to arid environments, have low photosynthesis rates, and higher water usage efficiencies. Plants in this category include cactus and succulents like pineapple. The CAM has evolved so that the initial CO₂ fixation can take

place in the dark with much less water loss than C3 or C4 pathways. CAM biomass also conserves carbon by recycling endogenously formed CO₂. CAM biomass species have not been exploited commercially for use as biomass feedstock.

Biomass Classification and Composition

Biomass can be classified into two major subdivisions, crop biomass and wood biomass. There are other sources of biomass, like waste from municipal areas and animal wastes, but these can be traced back to the two major sources. Biomass is composed of mainly three components, cellulose, hemicelluloses and lignin. The minor constituents of biomass are proteins, ash, starch, and other non-carbohydrate compounds. Table 3 gives the composition of some biomass species based on these components. RDF is the combustible fraction of municipal solid waste. Table 4 gives the heating value and carbon content in selected biomass components. The following section discusses the different components in biomass that will be referred to in latter sections of the report.

Starch: Starch is a polymer of glucose as the monomeric unit. It is a mixture of α -amylose and amylopectin as shown in Figure 9. Alpha-amylose is a straight chain of glucose molecules joined by α -1,4-glycosidic linkages. Amylopectin is similar to amylose except that short chains of glucose molecules branch off from the main chain (backbone). Starches found in nature are 10-30% α -amylose and 70-90% amylopectin. The α -1,4-glycosidic linkages are relatively bent and prevent the formation of sheets and subsequent layering of polymer chains. As a result, starch is soluble in water and relatively easy to break down into utilizable sugar units.

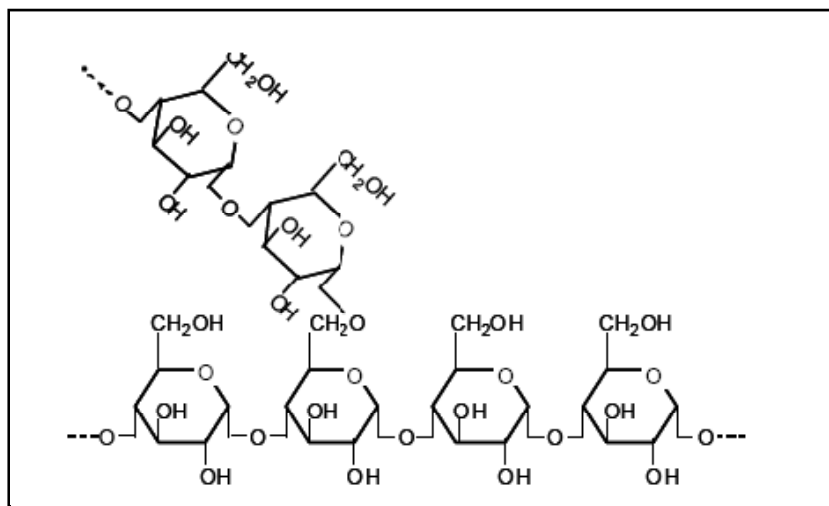


Figure 9 Structure of Starch (Paster et al., 2003)

Lignocellulosic Biomass: The non-grain portion of biomass (e.g., cobs, stalks), often referred to as agricultural stover or residues, and energy crops such as switchgrass are known as lignocellulosic biomass resources (also called cellulosic). These are comprised of cellulose, hemicellulose, and lignin (Paster et al., 2003). Generally, lignocellulosic material contains 30-50% cellulose, 20-30% hemicellulose, and 20-30% lignin. Some exceptions to this are cotton

(98% cellulose) and flax (80% cellulose). Lignocellulosic biomass is considered to be an abundant resource for the future bio-industry. Recovering the components in a cost-effective way requires pretreatment processes and discussed in later section.

Cellulose: Cellulosic biomass comprises 35-50% of most plant material. Cellulose is a polymer of glucose of degree of polymerization of 1000 to 10,000. Cellulose is a linear unbranched polymer of glucose joined together by β -1,4-glycosidic linkages as shown in Figure 10. Cellulose can either be crystalline or amorphous. Hydrogen bonding between chains leads to chemical stability and insolubility and serves as a structural component in plant walls (Paster et al., 2003). Lignocellulosic materials as they are found in nature are much more resistant than starch to acid and enzymatic hydrolysis due to the high degree of crystallinity of cellulose. As the core structural component of biomass, cellulose is also protected from environmental exposure by a sheath of lignin and hemicellulose. Extracting the sugars of lignocellulosics therefore involves a pretreatment stage to reduce the recalcitrance (resistance) of the biomass to cellulose hydrolysis.

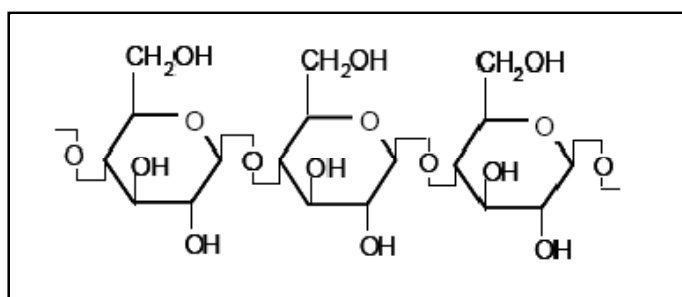


Figure 10 Structure of Cellulose (Paster et al., 2003)

Hemicellulose: Hemicellulose is a polymer containing primarily 5- carbon sugars such as xylose and arabinose with some glucose and mannose dispersed throughout as shown in Figure 11 (Paster et al., 2003). It forms a short chain polymer that interacts with cellulose and lignin to form a matrix in the plant wall, thereby strengthening it. Hemicellulose is more easily hydrolyzed than cellulose. Much of the hemicellulose in lignocellulosic materials is solubilized and hydrolyzed to pentose and hexose sugars during the pretreatment stage. Some of the hemicellulose is too intertwined with the lignin to be recoverable.

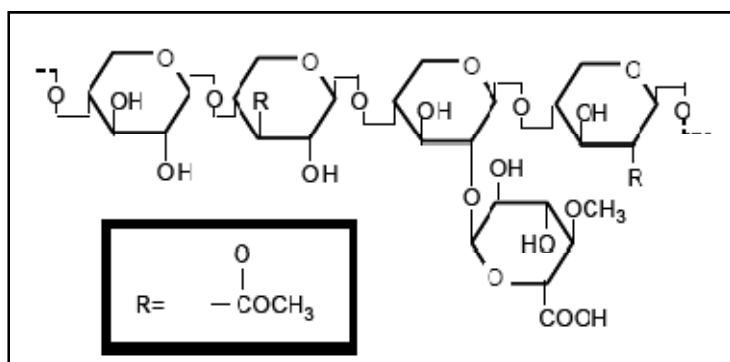


Figure 11 Structure of Hemicelluloses (Paster et al., 2003)

Table 3 Component percentage in representative biomass species (Klass, 1998)

Biomass type	Marine	Fresh water	Herbaceous	Woody	Woody	Woody	Waste
Name	Giant brown kelp	Water hyacinth	Bermuda grass	Poplar	Sycamore	Pine	RDF
Component (dry wt %)							
Celluloses	4.8	16.2	31.7	41.3	44.7	40.4	65.6
Hemicelluloses	--	55.5	40.2	32.9	29.4	24.9	11.2
Lignins	--	6.1	4.1	25.6	25.5	34.5	3.1
Mannitol	18.7	--	--	--	--	--	--
Algin	14.2	--	--	--	--	--	--
Laminarin	0.7	--	--	--	--	--	--
Fucoidin	0.2	--	--	--	--	--	--
Crude protein	15.9	12.3	12.3	2.1	1.7	0.7	3.5
Ash	45.8	22.4	5.0	1.0	0.8	0.5	16.7
Total	100.3	112.5	93.3	102.9	102.1	101.0	100.1

Table 4 Carbon weight % and heating value of biomass components (Klass, 1998)

Component	Carbon (wt %)	Higher heating value (MJ/kg)
Monosaccharides	40	15.6
Disaccharides	42	16.7
Polysaccharides	44	17.5
Crude proteins	53	24.0
Lignins	63	25.1
Lipids	76–77	39.8
Terpenes	88	45.2
Crude carbohydrates	41–44	16.7–17.7
Crude fibers	47–50	18.8–19.8
Crude triglycerides	74–78	36.5–40.0

Lignin: Lignin helps bind the cellulose/hemicelluloses matrix while adding flexibility to the mixture. The molecular structure of lignin polymers is very random and disorganized and consists primarily of carbon ring structures (benzene rings with methoxyl, hydroxyl, and propyl groups) interconnected by polysaccharides (sugar polymers) as shown in Figure 12. The ring structures of lignin have great potential as valuable chemical intermediates, mainly aromatic compounds. However, separation and recovery of the lignin is difficult. It is possible to break the lignin-cellulose-hemicellulose matrix and recover the lignin through treatment of the lignocellulosic material with strong sulfuric acid. Lignin is insoluble in sulfuric acid, while cellulose and hemicellulose are solubilized and hydrolyzed by the acid. However, the high acid concentration promotes the formation of degradation products that hinder the downstream utilization of the sugars. Pyrolysis can be used to convert the lignin polymers to valuable products, but separation techniques to recover the individual chemicals are lacking. Instead, the pyrolyzed lignin is fractionated into a bio-oil for fuels and high phenolic content oil which is used as a partial replacement for phenol in phenol-formaldehyde resins.

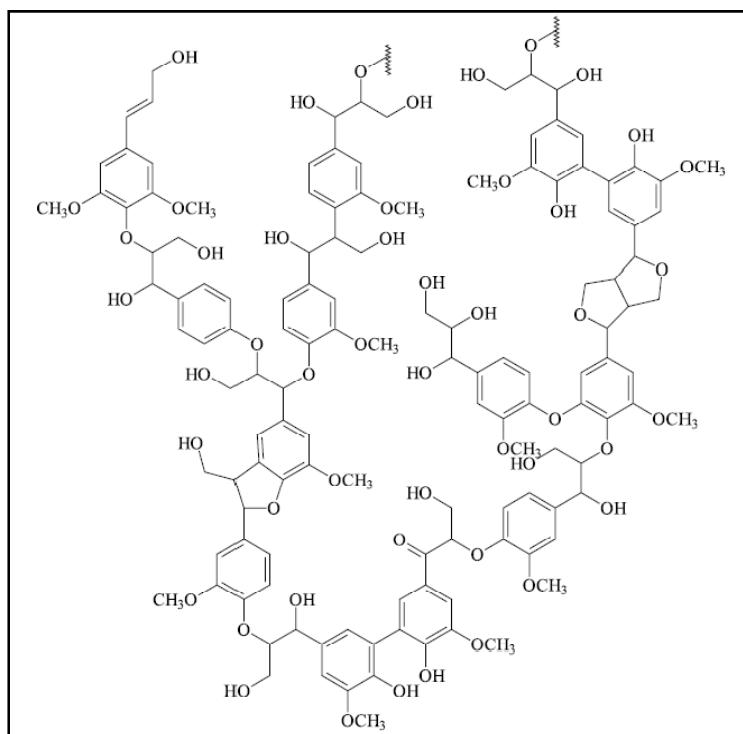


Figure 12 Structure of Lignin (Crocker et al.,2006)

Lipids, Fats and Oils: Oils can be obtained from oilseeds like soybean, canola etc. Vegetable oils are composed primarily of triglycerides, also referred to as triacylglycerols. Triglycerides contain a glycerol molecule as the backbone with three fatty acids attached to glycerol's hydroxyl groups. The chemical synthesis of a triglyceride is shown in Figure 13. In this example, the three fatty acids are all lauric acid, but could be a mixture of two or more fatty acids. Fatty acids differ in chain length and degree of condensation. The fatty acid profile and the double bonds present determine the property of the oil. These can be manipulated to obtain

certain performance characteristics. In general, the greater the number of double bonds, the lower the melting point.

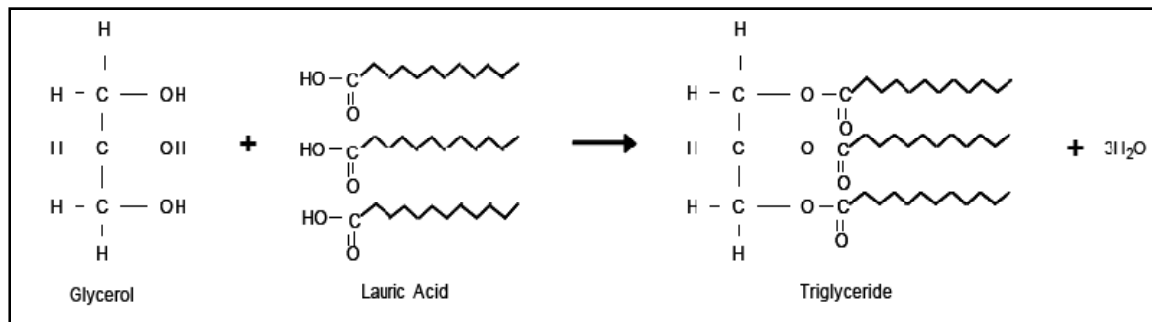


Figure 13 Formation of Triglycerides (Paster et al., 2003)

Feedstock Availability

Biomass availability in United States

The biomass feedstock availability for use in energy and bioproducts in the United States is given by Perlack et al., 2005. The biomass resources can be broadly classified as forest resources and agricultural resources. According to this report, 368 million dry tons of sustainable removable biomass could be produced on forestlands, and about 998 million dry tons could come from agricultural lands. The biomass resource potentials identified above are projected for the future with changes in land use and agricultural and forestry practices.

According to the report by Perlack et al., 2005, forestlands in the United States projects the production of 368 million dry tons annually of biomass. This projection includes 52 million dry tons of fuel wood harvested from forests, 145 million dry tons of residues from wood processing mills and pulp and paper mills, 47 million dry tons of urban wood residues including construction and demolition debris, 64 million dry tons of residues from logging and site clearing operations, and 60 million dry tons of biomass from fuel treatment operations to reduce fire hazards. All of these forest resources are sustainably available on an annual basis. For estimating the residue tonnage from logging and site clearing operations and fuel treatment thinning, a number of important assumptions were made:

- All forestland areas not currently accessible by roads were excluded
- All environmentally sensitive areas were excluded
- Equipment recovery limitations were considered
- Recoverable biomass was allocated into two utilization groups – conventional forest products and biomass for bioenergy and biobased products.

From agricultural lands, the report projects that United States can produce nearly 1 billion dry tons of biomass annually and still continue to meet food, feed, and export demands (Perlack et al., 2005). This projection includes 428 million dry tons of annual crop residues, 377 million dry tons of perennial crops, 87 million dry tons of grains, and 106 million dry tons of animal manures, process residues, and other miscellaneous feedstocks. Important assumptions that were made include the following:

- Yields of corn, wheat, and other small grains were increased by 50 percent
- The residue-to-grain ratio for soybeans was increased to 2:1
- Harvest technology was capable of recovering 75 percent of annual crop residues (when removal is sustainable)
- All cropland was managed with no-till methods
- 55 million acres of cropland, idle cropland, and cropland pasture were dedicated to the production of perennial bioenergy crops
- All manure in excess of that which can applied on-farm for soil improvement under anticipated EPA restrictions was used for biofuel
- All other available residues were utilized.

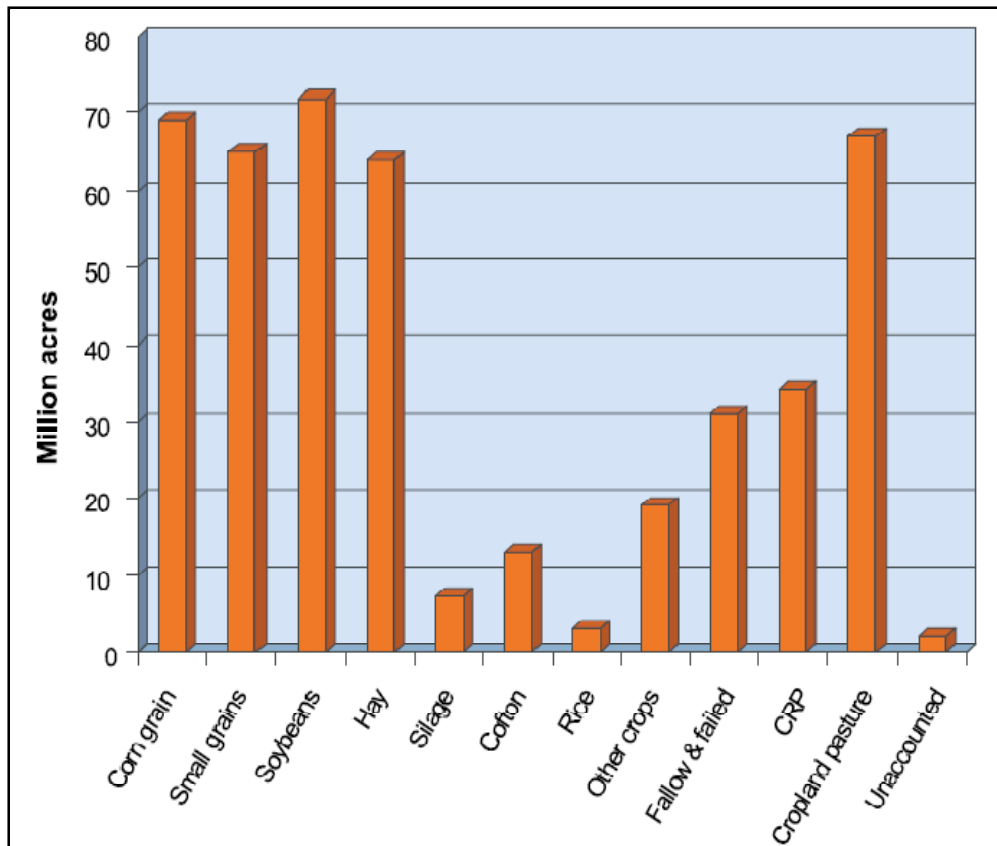


Figure 14 Agricultural Land Use in United States, Perlack et al., 2005

The land resource for biomass production in the United States from agricultural lands is given in Figure 14. The agricultural land totaled 455 million acres in 1997 — 349 million acres of land in active use to grow crops, 39 million acres of idle cropland, and 67 million acres of cropland used as pasture (Perlack et al., 2005). Grains and oilseeds are the major feedstock for byproducts manufacture. 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). The report by Perlack et al., 2005 studies the availability of crop biomass under three scenarios. These scenarios are the given below.

Current availability of biomass feedstocks from agricultural land: The current availability scenario studies biomass resources current crop yields, tillage practices (20-40 percent no-till for major crops), residue collection technology (~40 percent recovery potential), grain to ethanol and vegetable oil for FAME and FAEE production, and use of secondary and tertiary residues on a sustainable basis. The amount of biomass currently available for bioenergy and bioproducts is about 194 million dry tons annually and is shown in Figure 15. This is about 16 percent of the 1.2 billion dry tons of plant material produced on agricultural land. It includes 113 million dry tons of crop residues, 15 million dry tons of grain (starch) used for ethanol production, 6 million dry tons of corn fiber, and 60 million dry tons of animal manures and residues (e.g., MSW and animal fats). The single largest source of this current potential is corn residues or corn stover, totaling close to 75 million dry tons.

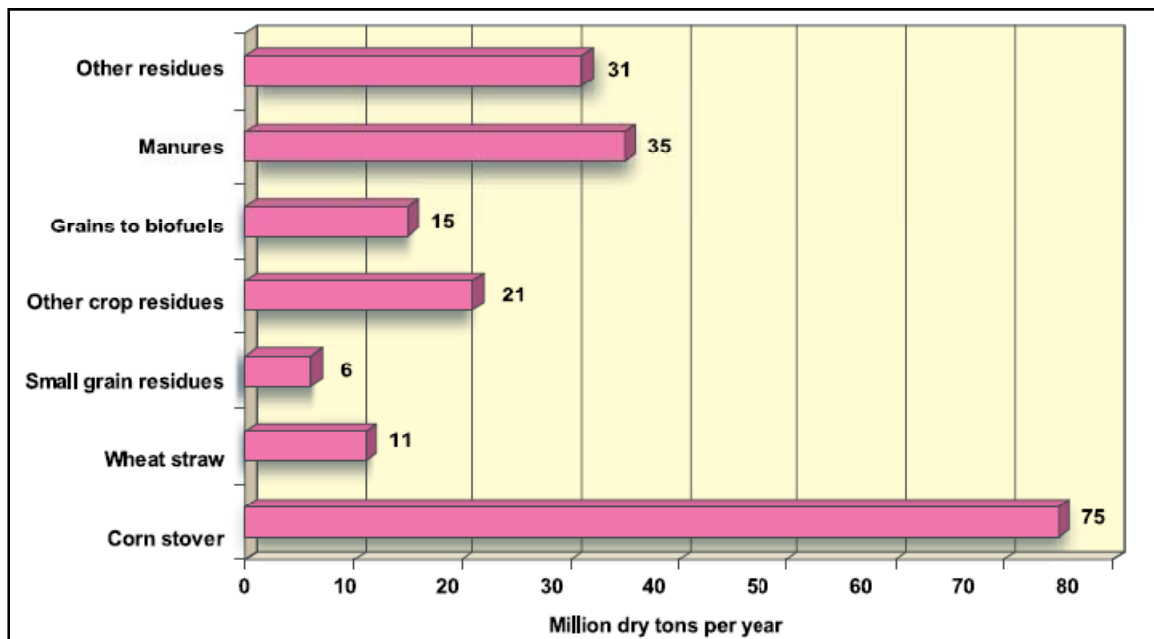


Figure 15 Current Availability of Biomass from Agricultural Lands, Perlack et al., 2005

Biomass availability through a combination of technology changes focused on conventional crops only: This scenario assumes an increase in crop yields for corn by 25-50 percent. Yields of wheat and other small grains, sorghum, soybeans, rice, and cotton are assumed to increase at rates lower than for corn. The rates and acres for each crop are fixed at levels predicted for 2014. Soybeans contribute no crop residue under a moderate yield increase of around 13% but make a small contribution with a high yield increase of about 23%. Collection equipment is assumed to be capable of recovering as much as 60% of residue under the moderate yield increases and 75% under the high yield increases but the actual removal amounts depend on the sustainability requirements. No-till cultivation is assumed to be practiced on

approximately 200 million acres under moderate yield increases and all of active cropland under high yields. The amount of corn and soybeans available for ethanol, FAME and FAEE production or other bioproducts was calculated by subtracting amounts needed to meet food requirements plus feed and export requirements from total quantities. All remaining grain was assumed to be available for bioproducts. Further, about 75 million dry tons of manure and other secondary and tertiary residues and wastes, and 50 percent of the biomass produced on CRP lands (17 to 28 million dry tons) are assumed to be available for bioenergy production. This intensive scenario for use of crop residue results in the annual production of 423 million dry tons per year under moderate yields and 597 million dry tons under high yields. In this scenario, about two-thirds to three-fourths of total biomass are from crop residues, as can be seen in Figure 16.

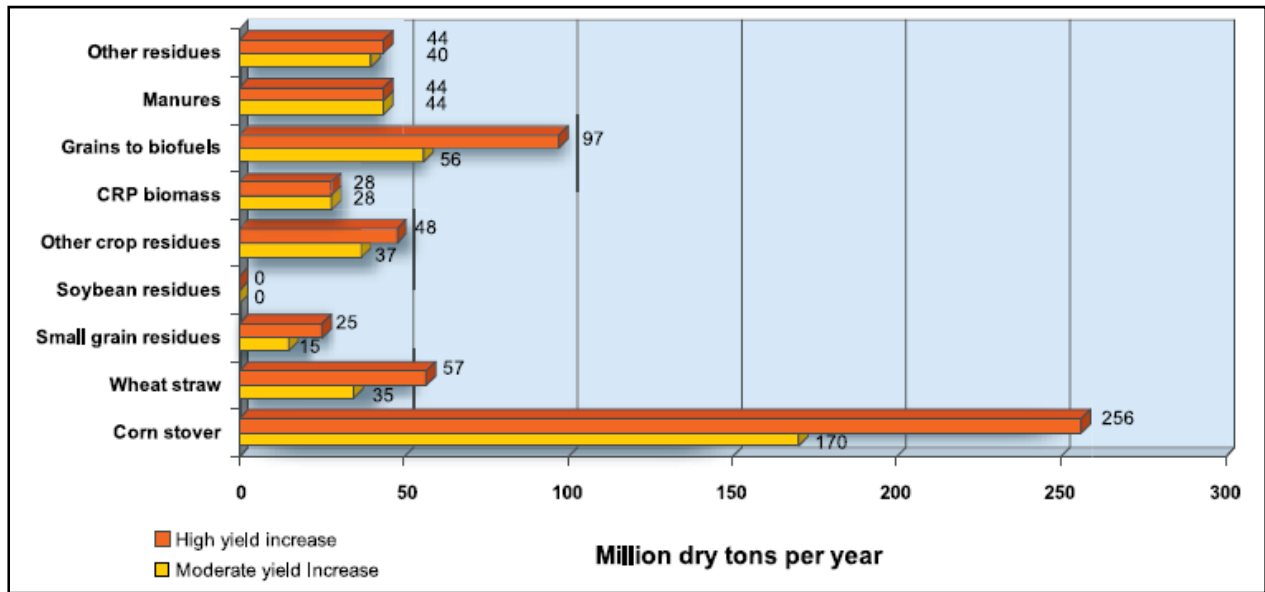


Figure 16 Availability of Biomass for Increased Crop Yields and Technology Changes, Perlack et al., 2005

Biomass availability through technology changes in both conventional crops and new perennial crops together with significant land use change: This scenario assumes the addition of perennial crops to the landscape, land use changes and changes in soybean varieties, as well as the technology changes assumed under the previous scenario. Soybean varieties are assumed to transition from an average residue-to-grain ratio of 1.5 to a ratio of 2.0 as current varieties are partially replaced with varieties that produce 50 to 100 percent more residue but maintain similar grain yields. The land use changes include the conversion of either 40 or 60 million acres to perennial crop production associated with moderate and high yield increases, respectively. Woody crops produced for fiber are expanded from 0.1 million acres to 5 million acres, where they can produce an average annual yield of 8 dry tons per acre. Twenty-five percent of the wood fiber crops are assumed to be used for bioenergy and the remainder for other, higher-value conventional forest products. Perennial crops (trees or grasses) grown primarily for bioenergy expand to either 35 million acres at 5 dry tons per acre per year or to 55 million acres with average yields of 8 dry tons per acre per year. Ninety-three percent of the perennial crops are assumed available for bioenergy and the remainder for other products. A small fraction of the

available biomass (10 percent) is assumed lost during the harvesting operations. This scenario results in the production of 581 to 998 million dry tons as shown in Figure 17. Crop residues increase even though conventional cropland is less because of the addition of more soybean residue together with increased yields. The single largest source of biomass is the crop residue, accounting for nearly 50 percent of the total produced. Perennial crops account for about 30 to 40 percent depending on the extent of crop yield increase (i.e., moderate or high).

Biomass availability in Louisiana

The biomass availability in Louisiana is given by the LSU AgCenter (de Hoope et al., 2006a, b). Louisiana, with its fertile soils and warm, moist climate, has potential to grow biomass for use as feedstock. Nearly half of its land is dedicated to growing timber. Additional land is used to raise agricultural crops. The forestry and agriculture industries combined contribute 7.0 percent of the gross state product. Many businesses use their wastes to be economical sources of fuel, although natural gas and other fossil fuels are readily available from local sources.

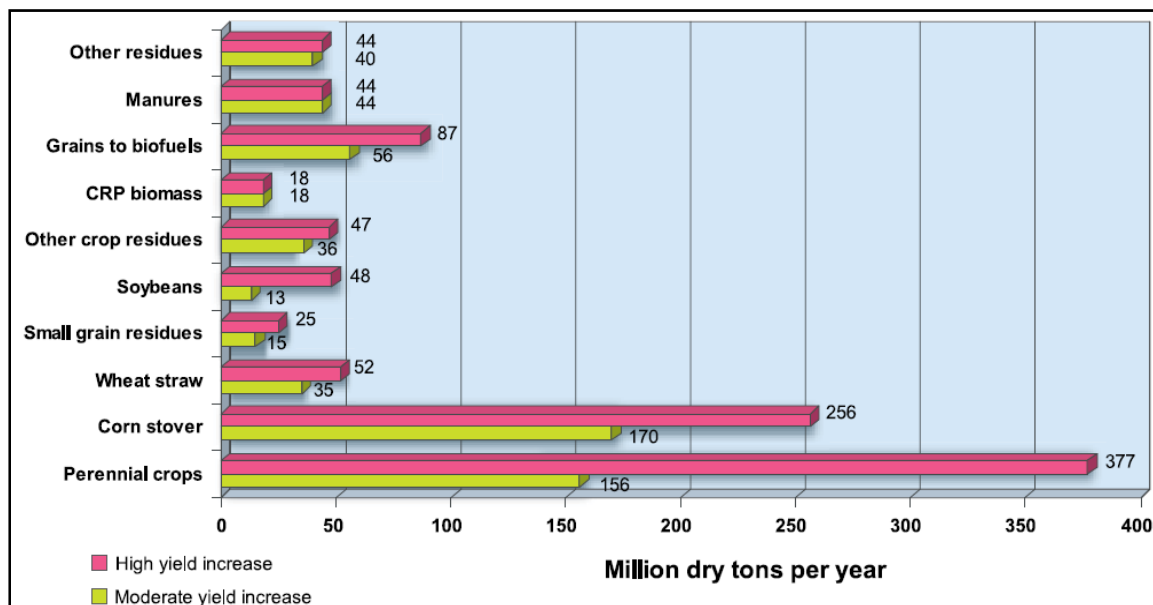


Figure 17 Availability of Biomass under Increased Crop Yields and Technology Changes, and Inclusion of Perennial Crops, Perlack et al., 2005

Louisiana’s forest products industry includes around a total of 100 sawmills plywood mills, panel mills, veneer mills and pulp/paper mills (de Hoope et al., 2006a). Together, they produce more than 7.0 million tons of wood residues annually, most of which are used by the industry for energy. Most mills utilize what they need for their own energy needs (such as lumber drying kilns or veneer driers) and sell the rest to other mills, usually to pulp and paper mills, which require a lot of energy and generate most of their own electricity. Even after this use, around 54,000 tons of residues annually are unused. Louisiana’s secondary forest products industry (cabinet shops, architectural millwork, furniture makers, pallet manufacturers, etc.) produces 80,000 tons of residues annually, including wood trimmings, sawdust and sander dust.

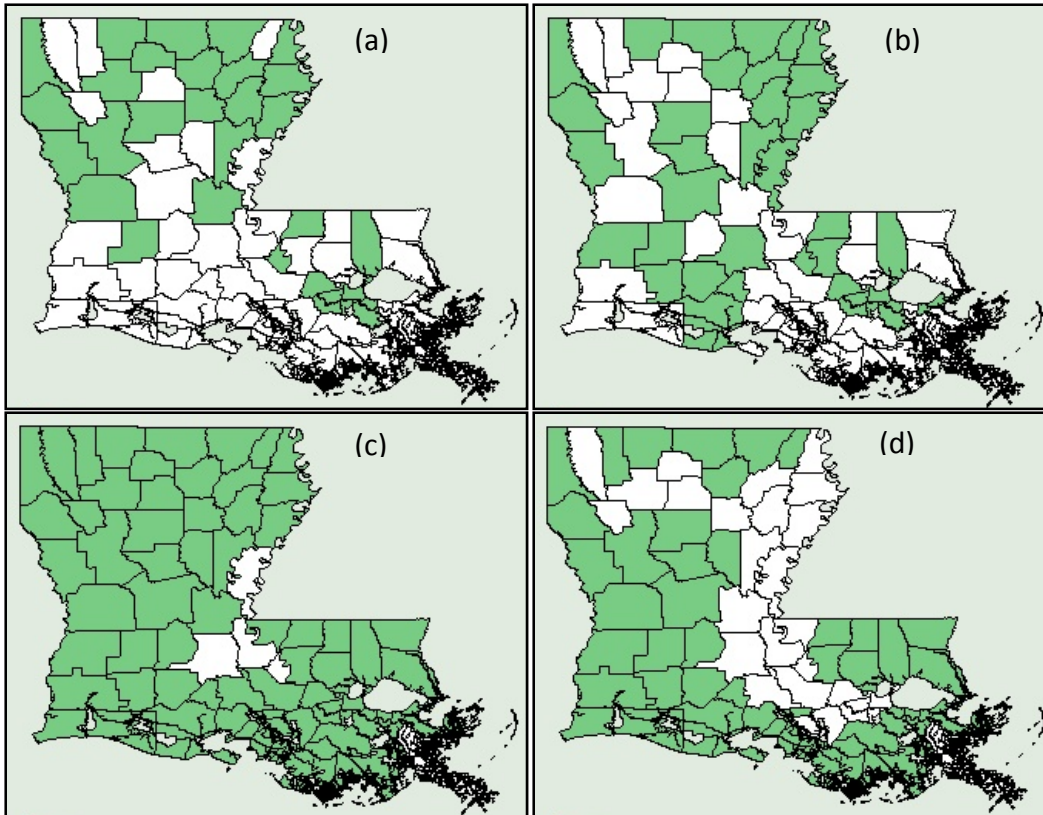


Figure 18. Crop distributions in Louisiana (a) Corn (b) Soybean (c) Sugarcane (d) Switchgrass (USDA, 2007)

Louisiana's agricultural industry is comprised of sugarcane, rice, soybean, corn and cotton fields (de Hoop et al., 2006a). The crop distributions in Louisiana are given in Figure 18. Their residues are used in various ways. Rice generates three types of residue: straw, hulls and bran. Rice straw is usually left in the fields during and after collection to prevent topsoil erosion. It is sometimes grazed by cattle or crawfish and then plowed back into the field for nutrients. Possible uses of rice hulls include compost, abrasives for polishing, additives in hand soap, conditioners for fertilizers, and energy. In winter, the bran is mixed with rice hulls to make cattle feed. About 96 percent of the bagasse produced by sugar mills is utilized, mostly as fuel to run the mills. Other uses include paper, ceiling tiles, industrial boards and compost. Soybean straw (stems) is usually left in the fields to prevent erosion. It also can be used as livestock bedding or burned for fuel. These residues can be alternately used as feedstock for the production of chemicals from fermentation, anaerobic digestion and gasification. Apart from agricultural and forest products, a huge quantity of municipal solid waste is found in Louisiana. Approximately 4.6 million tons of municipal solid waste is generated each year in Louisiana. 50% of this waste comprises of paper and wood. Another 8-10 million tons per year of industrial waste is generated in forms such as plastic, gypsum and sludge. Municipal waste can be used in anaerobic digesters to produce biogas and carboxylic acids. Kebanli, et al., 1981 gives a process that produces biogas via anaerobic digestion of animal waste and Thakanoses et al., 2003 gives a process to produce carboxylic acids and mixed alcohols.

Total Louisiana farmland peaked at 12,200,000 acres in the mid 1950's and has steadily declined over the years as farms became fewer and larger (de Hoope et al., 2006b). The 2006 acreage of crops harvested in Louisiana farms and their unit prices are given in Table 5. The total waste generated in Louisiana in different sectors is given in Table 6.

Table 5 Crop acreage and unit prices in Louisiana for 2006 (LSU AgCenter, 2007a,b)

Crop	Acreage	Total Production (in 2006)	Unit Price
Corn (Grain)	304,919	39,066,760 bu.	\$2.65/bu.
Sweet Corn	1,410	462,310 doz. ears	\$3.50/doz. ears
Rice	347,199	20,340,738 cwt.	\$8.90/cwt.
Soybeans	866,826	30,035,412 bu.	\$5.86/bu.
Sugarcane	400,308	2,536,944,346 lbs. (raw sugar) 76,113,677 gal. (molasses)	\$0.12/lb. \$0.20/gal.
Beets	51	14,908 doz. Bunches	\$7.00/doz. bunches
Wheat	110,767	6,308,015 bu.	\$4.01/bu.
Hay (grass and alfalfa)	258,350	555,551 tons (grass) 535 tons (alfalfa)	\$108.57/ton \$92.40/ton
Sorghum	85,734	6,969,078 cwt.	\$4.69/cwt.
1 bu.(bushel) = 56 lbs (corn); 60 lbs (soybeans); 56 lbs (sorghum); 60 lbs (wheat) 1 cwt. (hundred weight) = 100 lbs 1 ton (metric ton) = 1000 kg = 2200 lbs			

Table 6 Waste biomass availability in Louisiana (adapted from de Hoope et al., 2006a)

Type of Residue/waste	Wet Tons
Residue Wood, Sawdust, trimmings, bark	134,323
Logging Slash	8,432,792
Soybeans Straw	1,501,071
Sugarcane Bagasse (dry wt.)	122,702
Rice Hulls (dry wt.)	85,100
Straw	2,180,694
Corn Stalks, roots, husks	350,043
Wheat Straw	320,064
Grain sorghum (milo) Residue	52,544
Animal Waste Cattle manure/biogas	9,881,919,000cf
Poultry manure	944,150
Oats Straw	267,670
Cotton Gin trash	57,553

New Feedstock Options – Algae

The previous section discussed conventional biomass feedstock options. Other organisms that undergo photosynthesis are cyanobacteria and algae. Of these, microalgae are the most efficient in photosynthesis, with 60-70% of each cell's volume capable of photosynthesis (Arnaud, 2008). The algae also do not have roots, stems or leaves, which diverts resources to produce hydrocarbons. Methods to cultivate algae have been developed over the years. Recent

developments in algae growth technology include vertical reactors (Hitchings, 2007) and bag reactors (Borne, 2007) made of polythene mounted on metal frames, eliminating the need for land use for cultivation. The NREL Aquatic Species Program (Sheehan et. al, 1998) mentions “raceway” ponds design for growth of algae. This method required shallow ponds built on land area and connected to a carbon dioxide source such as a power plant. Productivity in these pond designs were few grams/m²/d. Other designs include tubular cultivation facilities and the semi-continuous batch cultures gave improved production rates of algae. For example, the 3D Matrix System of Green Fuel Technologies Corporation have an average areal productivity of 98g/m²/d (ash free, dry weight basis), with highs of over 170 g/m²/d achieved during a run time of 19 days. Dry algae factor is the percentage of algae cells in relation with the media where is cultured, e.g. if the dry algae factor is 50%, one would need 2 kg of wet algae (algae in the media) to get 1 kg of algae cells. Lipid factor is the percentage of vegoil in relation with the algae cells needed to get it, i.e. if the algae lipid factor is 40%, one would need 2.5 kg of algae cells to get 1 kg of oil.



Figure 19 Algae Production from Power Plant Exhaust (Borne, 2007)

Algae have the potential for being an important source of oil and carbohydrates for chemicals as shown in Figure 19. Yields of 15, 000 gallons/acre per year of oil have been obtained and this compares to 60 gallons/acre per year for soybeans. They can be grown on power plant exhaust as shown in Figure 19. GreenFuel Technologies has developed a process that grows algae in plastic bags using CO₂ from smokestacks via naturally occurring species of algae. The CO₂ source can also come from fermentation or geothermal gases. Algae can be converted to transportation fuels and feed ingredients or recycled back to a combustion source as biomass for power generation. Industrial facilities do not need any internal modifications to host a GreenFuel algae farm. In addition, the system does not require fertile land or potable water. Water used can be recycled and waste water can be used as compared to oilseed crops’ high water demand. With high growth rates, algae can be harvested daily. Bags of algae are shown at the Redhawk power plant near Phoenix, Arizona which are reported to be absorbing carbon dioxide while producing 5,000 gallons of biodiesel an acre each year (Borne, 2007).

A vertical reactor system is being developed by Valcent Products, Inc of El Paso, Texas (www.valcent.net) using the 340 annual days of sunshine and carbon dioxide available from power plant exhaust as shown in Figure 20 (Hitchings, 2007). Research is underway to determine the species of algae for oil production and the best method of extracting the oil. Extraction methods being evaluated include expeller/press, hexane solvent extraction and supercritical fluid extraction and are the more costly step in the process.

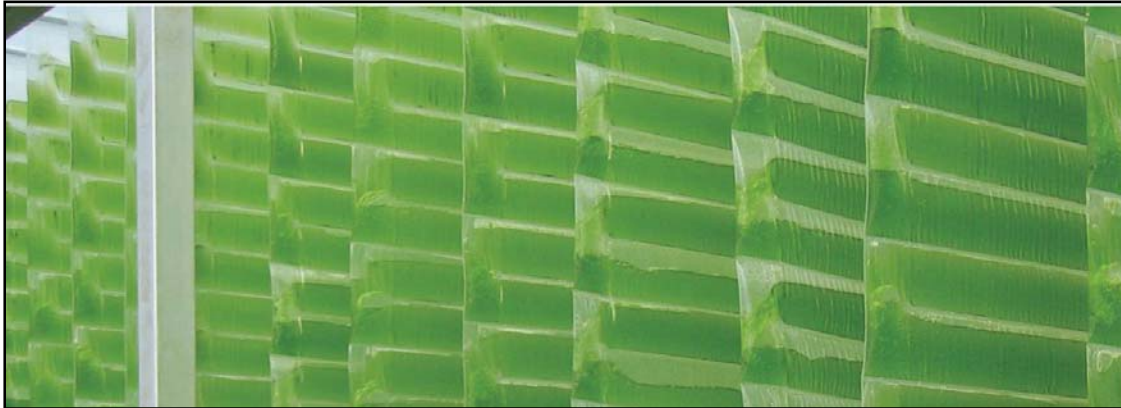


Figure 20 Vertical Algae Reactor from Power Plant Exhaust (Hitchings, 2007).

“Raceway” Design for algae growth included shallow ponds in which the algae, water and nutrients circulate around a “racetrack” as shown in Figure 21. Paddlewheels provide the flow to keep algae suspended in water. Algae are circulated back up to the surface on a regular frequency. The limited depth of shallow ponds keeps the algae exposed to sunlight. The ponds are operated continuously; that is, water and nutrients are constantly fed to the pond, while algae-containing water is removed at the other end. Some kind of harvesting system is required to recover the algae, which contains substantial amounts of natural oil.

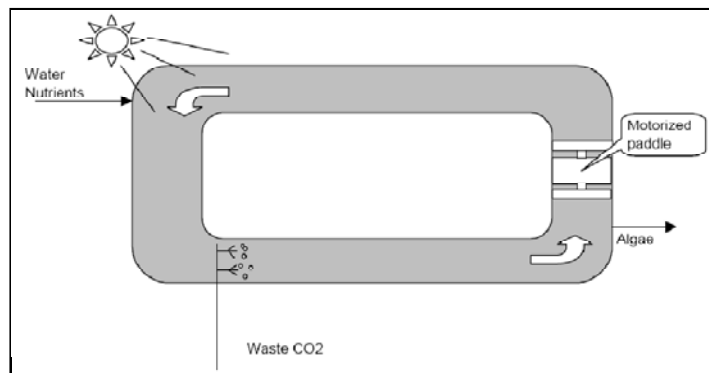


Figure 21 “Raceway” designs for Algae production (Sheehan et. al, 1998)

The concept of the raceway design for algae growth can be extended to an algae farm as shown in Figure 22. This consists of numerous ponds similar to the raceway in which algae is grown and harvested. The size of these ponds is measured in terms of surface area (as opposed to volume) as the surface area is critical to capturing sunlight. The productivity is measured in

terms of biomass produced per day per unit of available surface area. These designs required large acres of land and thus obtained the scale of farms.

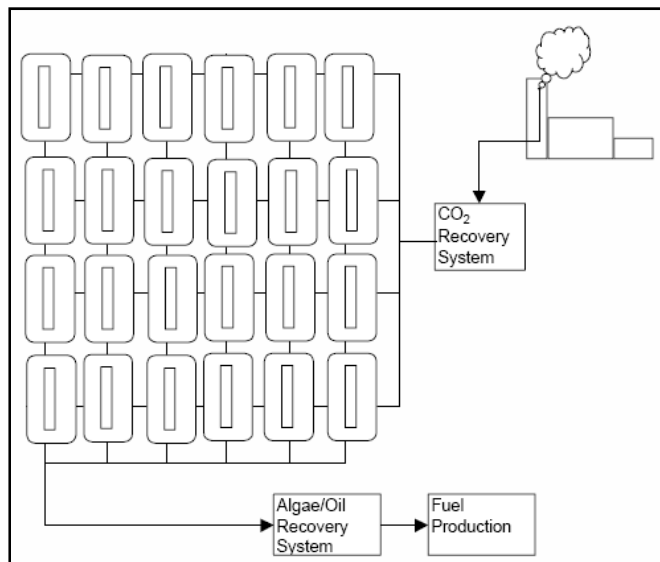


Figure 22 algae farm

Enhanced Biofuel Technology, A2BE Carbon Capture LLC are some of the firms that use the concept of raceway pond design and algae farm for production of algae for biofuels.

Algae are plant-like microorganisms that preceded plants in developing photosynthesis, the ability to turn sunlight into energy (www.microbeworld.org). Algae range from small, single-celled organisms to multi-cellular organisms, some with fairly complex differentiated form. Algae are usually found in damp places or bodies of water and thus are common in terrestrial as well as aquatic environments. Like plants, algae require primarily three components to grow: sunlight, carbon-di-oxide & water. Algae cells contain light-absorbing chloroplasts and produce oxygen through photosynthesis. Biologists have categorized microalgae in a variety of classes, mainly distinguished by their pigmentation, life cycle and basic cellular structure. The four most important (in terms of abundance) are (Sheehan et. al, 1998):

- The diatoms (Bacillariophyceae): These algae dominate the phytoplankton of the oceans, but are also found in fresh and brackish water. Approximately 100,000 species are known to exist. Diatoms contain polymerized silica (Si) in their cell walls. All cells store carbon in a variety of forms. Diatoms store carbon in the form of natural oils or as a polymer of carbohydrates known as chrysolaminarin.
- The green algae (Chlorophyceae): These type of algae are abundant in freshwater, for example, in a swimming pool. They can occur as single cells or as colonies. Green algae are the evolutionary progenitors of modern plants. The main storage compound for green algae is starch, though oils can be produced under certain conditions.
- The blue-green algae (Cyanophyceae): This type of algae is closer to bacteria in structure and organization. These algae play an important role in fixing nitrogen from the atmosphere. There are approximately 2,000 known species found in a variety of habitats.

- The golden algae (Chrysophyceae): This group of algae is similar to the diatoms. They have more complex pigment systems, and can appear yellow, brown or orange in color. Approximately 1,000 species are known to exist, primarily in freshwater systems. They are similar to diatoms in pigmentation and biochemical composition. The golden algae produce natural oils and carbohydrates as storage compounds.

U.S. Department of Energy's Office of Fuels Development funded a program to develop renewable transportation fuels from algae (Sheehan et. al, 1998). The program initially looked into over 3,000 strains of organisms, which was then narrowed down to about 300 species of micro organisms. The program concentrated not only on algae that produced a lot of oil, but also with algae that grow under severe conditions—extremes of temperature, pH and salinity.

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). *Botryococcus braunii* species of algae has been engineered to produce the terpenoid C₃₀ botryococcene, a hydrocarbon similar to squalene in structure (Arnaud, 2008). The species has been engineered to secrete the oil, and the algae can be reused in the bioreactor. A further modification to the algae is smaller light collecting antennae, allowing more light to penetrate the algae in a polythene container reactor system. A gene, *tlal*, is responsible for the number of chlorophyll antennae, can be modified to reduce the chlorophyll molecules from 600 to 130. Botryococcene is a triterpene, and unlike triglycerides, cannot undergo transesterification. It can be used as feedstock for hydrocracking in an oil refinery to produce octane, kerosene and diesel. Upto 86% of its dry weight can be long chain hydrocarbons (Wikipedia, 2008).

Carbon dioxide sources for algae growth can be from pipelines for CO₂, flue gases from power plants or any other sources rich in carbon dioxide. The flue gases from power plants were previously not considered as suitable algae cultivation land was not found near power plants. However, with newer designs of algae reactors as those shown in Figures 19 and 20 are developed, the flue gases are becoming suitable sources for algae cultivation. Water usage for algae growth is a major concern. In an open pond system, the loss of water is greater than in closed tubular cultivation or bag cultivation methods. The water can be local industrial water and recycled after harvesting algae.

Microalgae contain lipids and fatty acids as membrane components, storage products, metabolites and sources of energy. Algae contain between 2% and 40% of lipids/oils by weight. Table 7 shows different compositions of various strains of algae.

Algae oils can be extracted using conventional oil extraction methods like Expeller/Press, Hexane solvent oil extraction and Supercritical Fluid extraction (www.oilgae.com). Approximately 70-75% of algae oil can be extracted using expeller press while 95% oil can be extracted by hexane solvent oil extraction and 100% oil extracted using supercritical fluid extraction.

Table 7 Protein, carbohydrate, lipids and nucleic acid composition of various strains of algae (Sheehan et. al, 1998).

Strain	Protein	Carbohydrates	Lipids	Nucleic acid
<i>Scenedesmus obliquus</i>	50-56	10-17	12-14	3-6
<i>Scenedesmus quadricauda</i>	47	-	1.9	-
<i>Scenedesmus dimorphus</i>	8-18	21-52	16-40	-
<i>Chlamydomonas reinhardtii</i>	48	17	21	-
<i>Chlorella vulgaris</i>	51-58	12-17	14-22	4-5
<i>Chlorella pyrenoidosa</i>	57	26	2	-
<i>Spirogyra sp.</i>	6-20	33-64	11-21	-
<i>Dunaliella bioculata</i>	49	4	8	-
<i>Dunaliella salina</i>	57	32	6	-
<i>Euglena gracilis</i>	39-61	14-18	14-20	-
<i>Prymnesium parvum</i>	28-45	25-33	22-38	1-2
<i>Tetraselmis maculata</i>	52	15	3	-
<i>Porphyridium cruentum</i>	28-39	40-57	9-14	-
<i>Spirulina platensis</i>	46-63	8-14	4-9	2-5
<i>Spirulina maxima</i>	60-71	13-16	6-7	3-4.5
<i>Synechococcus sp.</i>	63	15	11	5
<i>Anabaena cylindrica</i>	43-56	25-30	4-7	-

Biomass Conversion Routes

The conversion of biomass to chemical products involves several steps. Typically, biomass conversion routes begin with pretreatment in case of cellulosic and grain biomass and extraction of oil in case of oilseeds. Then the cellulosic or starch containing biomass undergoes fermentation (anaerobic or aerobic), gasification or pyrolysis. The oil in oilseeds is transesterified to obtain fatty acids. These conversion processes are reviewed in the following sections.

Biomass Pretreatment

Biomass is primarily composed of cellulose, hemicelluloses and lignin. The cellulose and hemicelluloses are polysaccharides of hexose and pentose. Any process that uses biomass needs to be pretreated so that the cellulose and hemicellulose in the biomass are broken down to their monomeric form. Pretreatment processes produce a solid pretreated biomass residue that is more amenable to enzymatic hydrolysis by cellulases and related enzymes than native biomass. Biocatalysts like yeasts and bacteria can act only on the monomers and ferment them to alcohols, lactic acid, etc. The pretreatment process also removes the lignin in biomass which is not acted upon by enzymes or fermented further.

Pretreatment usually begins with a physical reduction in the size of plant material by milling, crushing and chopping (Teter et al., 2006). For example, in the processing of sugarcane, the cane is first cut into segments and then fed into consecutive rollers to extract cane juice rich in sucrose and physically crush the cane, producing a fibrous bagasse having the consistency of

sawdust. In the case of corn stover processing, the stover is chopped with knives or ball milled to increase the exposed surface area and improve wettability.

After the physical disruption process, the biomass may be chemically treated to remove lignin (Teter et al., 2006). Lignin forms a coating on the cellulose microfibrils in untreated biomass, thus making the cellulose unavailable for enzyme or acid hydrolysis. Lignin also absorbs some of the expensive cellulose-active enzymes.

The following pretreatment processes are employed for biomass conversion:

Hot Wash Pretreatment: The hot wash pretreatment process involves the passage of hot water through heated stationary biomass and is responsible for solubilization of the hemicellulose fraction (Teter et al., 2006). The hemicellulose is converted to pentose oligomers by this process which needs to be further converted to respective monosaccharides before fermentation. The performance of this pretreatment process depends on temperature and flow rate, requiring about 8-16 minutes. About 46% of lignin is removed at high rates and temperatures. The hydrothermal process does not require acid resistant material for the reactors, but water use and recovery costs are disadvantages to the process.

Acid Hydrolysis: Hydrolysis is a chemical reaction or process where a chemical compound reacts with water. The process is used to break complex polymer structures into its component monomers. The process can be used for the hydrolysis of polysaccharides like cellulose and hemicelluloses (Katzen et al., 2006). When hydrolysis is catalyzed by the presence of acids like sulfuric, hydrochloric, nitric or hydrofluoric acids, the process is called acid hydrolysis. The reactions for hydrolysis can be expressed by Equations 2 and 3.



The desired products of hydrolysis are the glucose and xylose. Under severe conditions of high temperature and acid concentrations, the product tends to HMF, furfural and the tars.

Dilute sulfuric acid is inexpensive in comparison to the other acids. It has also been studied and the chemistry well known for acid conversion processes (Katzen et al., 2006). Biomass is impregnated with a dilute sulfuric acid solution and treated with steam at temperatures ranging 140-260 °C. Xylan is rapidly hydrolyzed to xylose at low temperatures of 140-180 °C. At higher temperatures cellulose is depolymerized to glucose and the xylan is converted to furfural and tars.

Concentrated acids at low temperatures (100-120 °C) are used to hydrolyze cellulose and hemicelluloses to sugars (Katzen et al., 2006). Higher yields of sugars are obtained in this case with lower conversion to tars. The viability of this process depends on low-cost recovery of expensive acid catalysts.

Enzymatic Hydrolysis: Acid hydrolysis explained in the previous section has a major disadvantage where the sugars are converted to degradation products like tars. This degradation can be prevented by using enzymes favoring 100% selective conversion of cellulose to glucose. When hydrolysis is catalyzed by such enzymes, the process is known as enzymatic hydrolysis (Katzen et al., 2006).

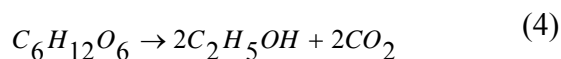
Enzymatic hydrolysis is carried out by microorganisms like bacteria, fungi, protozoa, insects etc. (Teter et al., 2006). Advancement of gene sequencing in microorganisms has made it possible to identify the enzymes present in them which are responsible for the biomass degradation. Bacteria like *Clostridium thermocellum*, *Cytophaga hutchinsonii*, *Rubrobacter xylanophilus* etc. and fungi like *Trichoderma reesei* and *Phanerochaete chrysosporium* have revealed enzymes responsible for carbohydrate degradation.

Based on their target material, enzymes are grouped into the following classifications (Teter et al., 2006). Glucanases or cellulases are the enzymes that participate in the hydrolysis of cellulose to glucose. Hemicellulases are responsible for the degradation of hemicelluloses. Some cellulases have significant xylanase or xyloglucanase side activity which makes it possible for use in degrading both cellulose and hemicelluloses.

Ammonia Fiber Explosion: This process uses ammonia mixed with biomass in a 1:1 ratio under elevated pressure (1.4-3 atm) at temperatures of 60-110 °C for 5-15 minutes, then explosive pressure release. The volatility of ammonia makes it easy to recycle the gas (Teter et al., 2006).

Fermentation

The pretreatment of biomass is followed by the fermentation process where pretreated biomass containing 5-carbon and 6-carbon sugars is catalyzed with biocatalysts to produce desired products. Fermentation refers to enzyme-catalyzed, energy-yielding chemical reactions that occur during the breakdown of complex organic substrates in presence of microorganisms (Klass, 1998). The microorganisms used for fermentation can be yeast or bacteria. The microorganisms feed on the sucrose or glucose released after pretreatment and convert them to alcohol and carbon dioxide. The simplest reaction for the conversion of glucose by fermentation is given in Equation 4.



In general, fermentation is an enzymatically controlled transformation of an organic compound. Enzyme controlled reactions have the advantage of being conducted under mild conditions with a degree of specificity. An enzyme catalyst is highly specific, catalyzes only one or a small number of reactions, and a small amount of enzyme is required. Enzymes are usually proteins of high molecular weight ($15,000 < MW < \text{several million Daltons}$) produced by living cells. The catalytic ability is due to the particular protein structure, and a specific chemical reaction is catalyzed at a small portion of the surface of an enzyme, called an active site (Lee, 1992).

Enzymes have been used since early human history without knowing how they worked. Enzymes have been used commercially since the 1890s when fungal cell extracts were used to convert starch to sugar in brewing vats. Many common organic chemicals can be manufactured using live organisms. A list of 82 of these chemicals going from acetic acid to zanaflo gums is given by Klass, 1998.

The largest volume chemical from fermentation is ethanol (C_2H_5OH) which reached a record 5.0 billion gallons in 2006 and consumed 20% of the U. S. corn crop (Johnson, 2007b). Approximately 90% of domestic ethanol is produced from starch in corn of which 85% is produced in five Midwestern states (Smith, 2005). The Renewable Fuels Association (RFA, 2006) reported that there are 35 new ethanol plans under construction and nine expansions which will raise the annual capacity by 2.2 billion gallons to 6.7 billion gallons annually (Hess, 2006a). If this trend and the existing and anticipated policy incentives in support of ethanol continue, U.S. ethanol production could reach 7 billion gallons in 2010, 3.3 billion gallons more than the amount produced in 2005 (ERS/USDA, 2006).

Anaerobic Digestion

Anaerobic digestion of biomass is the treatment of biomass with a mixed culture of bacteria to produce methane (biogas) as a primary product. The four stages of anaerobic digestion are hydrolysis, acidogenesis, acetogenesis and methanogenesis.

In the first stage, hydrolysis, complex organic molecules are broken down into simple sugars, amino acids, and fatty acids with the addition of hydroxyl groups. In the second stage, acidogenesis, volatile fatty acids (e.g., acetic, propionic, butyric, valeric) are formed along with ammonia, carbon dioxide and hydrogen sulfide. In the third stage, acetogenesis, simple molecules from acidogenesis are further digested to produce carbon dioxide, hydrogen and organic acids, mainly acetic acid. Then in the fourth stage, methanogenesis, the organic acids are converted to methane, carbon dioxide and water.

Anaerobic digestion can be conducted either wet or dry where dry digestion has a solids content of 30% or greater and wet digestion has a solids content of 15% or less. Either batch or continuous digester operations can be used. In continuous operations, there is a constant production of biogas while batch operations can be considered simpler and the production of biogas varies.

The standard process for anaerobic digestion of cellulose waste to biogas (65% methane-35% carbon dioxide) uses a mixed culture of mesophilic or thermophilic bacteria. Mixed cultures of mesophilic bacteria function best at 37°-41°C and thermophilic cultures function best at 50°-52°C for the production of biogas. Biogas also contains small amount of hydrogen with a trace of hydrogen sulfide, that is usually used to produce electricity. There are two by-products of anaerobic digestion: acidogenic digestate and methanogenic digestate. Acidogenic digestate is a stable organic material comprised largely of lignin and chitin resembling domestic compost, and it can be used as compost or to make low grade building products such as fiberboard. Methanogenic digestate is a nutrient rich liquid, and it can be used as a fertilizer but may include

low levels of toxic heavy metals or synthetic organic materials such as pesticides or PCBs, depending on the source of the biofeedstock.

Kebanli, et al., 1981 gives a detailed process design along with pilot unit data for converting animal waste to fuel gas which is used for power generation. A process flow diagram is shown in Figure 23. A first order rate constant, $0.011 \pm 0.003 \text{ day}^{-1}$, was measured for the conversion of volatile solids to biogas from dairy farm waste. In a biofeedstock, the total solids are the sum of the suspended and dissolved solids, and the total solids are composed of volatile and fixed solids. Volatile solids are organic compounds that can be treated by biological processes, and their concentrations are measured by procedures given in Standard Methods, 1976.

In general, the residence time for an anaerobic digester varies with the amount of feed material, type of material and the temperature. Residence time of 15-30 days is typical for mesophilic digestion, and residence time for thermophilic digestion is about one-half of that for mesophilic digestion. The digestion of the organic material involves a mixed culture of naturally occurring bacteria, each performing a different function. Maintaining anaerobic conditions and a constant temperature are essential for the viability of the bacterial culture. A review is given by Pike, et al., 1979, of process equipment, operating conditions, feedstock, methane generation rate and volatile solids reduction for generation of fuel gas from cellulose wastes.

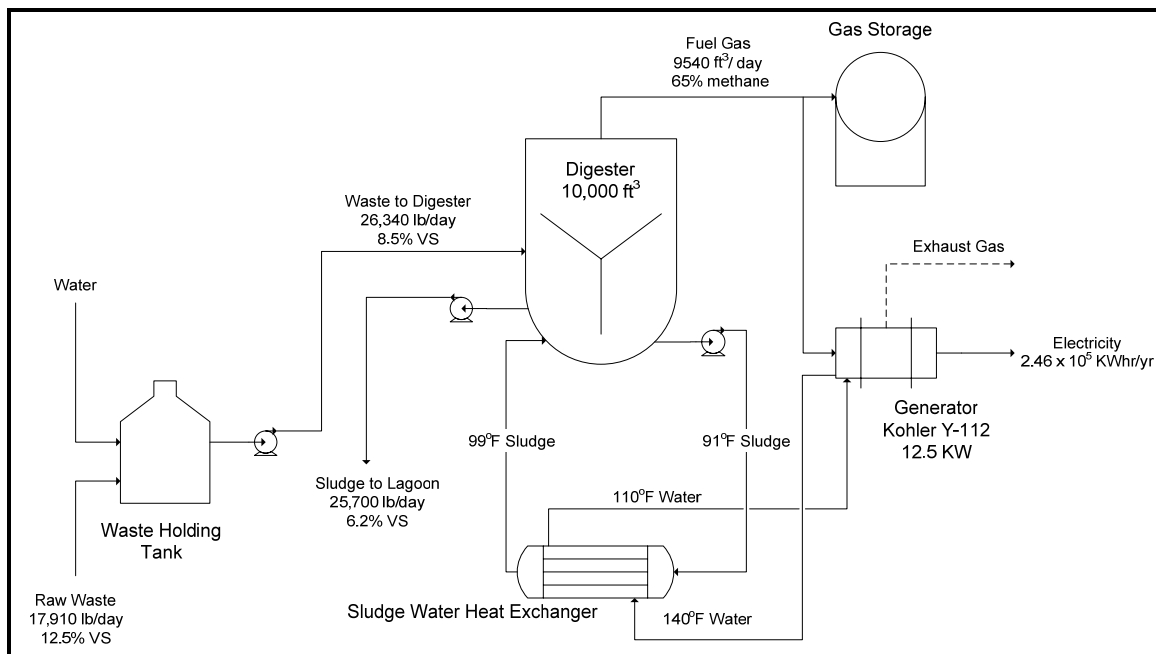


Figure 23. Process Flow Diagram of Anaerobic Digestion of Animal Waste (Kebanli, et al., 1981).

Thanakoses et al., 2003 describes a modification of the anaerobic digestion process, the MixAlco process, where corn stover and pig manure are converted to carboxylic acids. In the MixAlco process, anaerobic digestion is used to produce mixed alcohols by inhibiting the fourth stage, methanogenesis, as shown in Figure 24. The conversion of the organic acids to methane,

carbon dioxide and water are inhibited using iodoform (CHI₃) and bromoform (CHBr₃). Biofeedstocks to this process can include urban wastes, such as municipal solid waste and sewage sludge, agricultural residues, such as corn stover and bagasse. Products include carboxylic acids (e.g., acetic, propionic, butyric acid), ketones (e.g., acetone, methyl ethyl ketone, diethyl ketone) and biofuels (e.g., ethanol, propanol, butanol). The process uses a mixed culture of naturally occurring microorganisms found in natural habitats such as the rumen of cattle. The microorganisms anaerobically digest biomass into a mixture of carboxylic acids during the acidogenic and acetogenic stages of anaerobic digestion. This process differs from the processes that use enzymes to convert starch and cellulose wastes to simple sugars which are converted to ethanol by yeast fermentation.

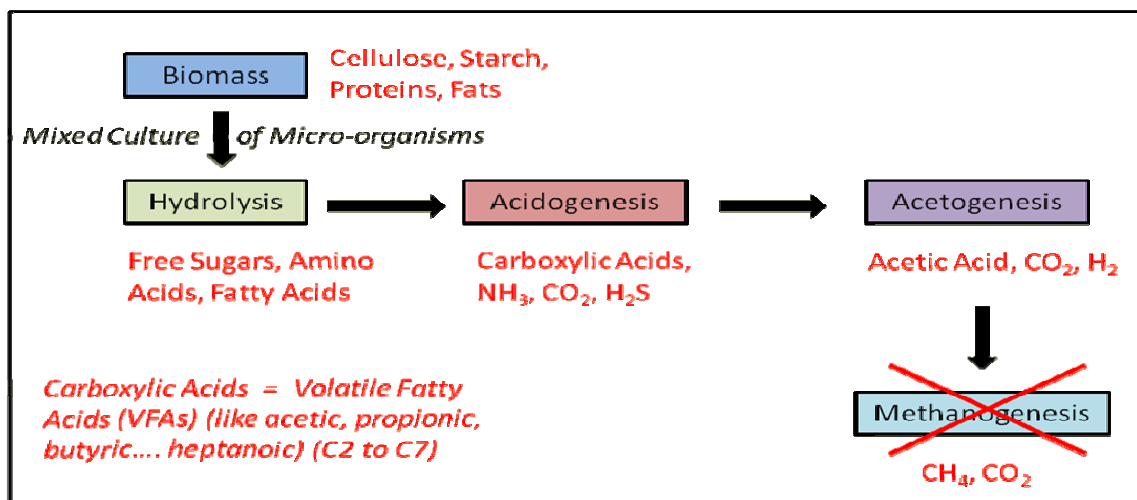


Figure 24 Production of Carboxylic Acids from Anaerobic Digestion (Granda, 2007)

Table 8 Carboxylic acid products at different culture temperatures (Granda, 2007)

Acid	40°C	55°C
C2 – Acetic	41 wt%	80 wt%
C3 – Propionic	15 wt%	4 wt%
C4 – Butyric	21 wt%	15 wt%
C5 – Valeric	8 wt%	< 1 wt%
C6 – Caproic	12 wt%	< 1 wt%
C7 – Heptanoic	3 wt%	< 1 wt%
	100 wt%	100 wt%

Granda, 2007 describes the MixAlco Process in details for the production of mixed alcohols, ketones and carboxylate salts. The process is outlined in Figure 25 where biomass is pretreated with lime to remove lignin. Calcium carbonate is also added to the pretreatment process. The biomass contains mainly waste biomass consisting of sugarcane bagasse, African millet straw, sorghum straw, tobacco stalks, etc. The resultant mixture containing hemicellulose and cellulose is fermented using a mixed culture of bacteria obtained from cattle rumen. This process produces a mixture of carboxylate salts which is then fermented. The fermentation

conditions of the MixAlco Process make it a viable process, since the fermentation involves mixed culture of bacteria obtained from animal rumen, which is available at lower cost compared to genetically modified organisms and sterile conditions required by other fermentation processes. Carboxylic acids are naturally formed in the following places: animal rumen, anaerobic sewage digestors, swamps, termite guts, etc. The carboxylic acids are preferred over alcohol in the process because the Gibbs' free energy is less for the formation of acid as shown in Equation 2-5 and 2-6. The acid distribution is given in Table 8.

(5)

(6)

Figure 25 Flow Diagram for the MixAlco Process using Anaerobic Digestion (Granda, 2007)

The MixAlco process proceeds to form carboxylate salts with the calcium carbonate. Dewatering process removes water. Then the carboxylate salts are thermally decomposed to mixed ketones like acetone, diethyl ketone and dipropyl ketones. The thermal conversion kinetics are given in Figure 26.

The mixed ketones can then be converted to ethanol by hydrogenation using Raney nickel catalyst at a temperature of 130°C and pressure of 12 atm in a stirred tank reactor for 35 minutes. The MixAlco process can be used for producing acetic acid in the proposed chemical production complex.

Aiello-Mazzarri et al., 2005 describes the production of carboxylic acids from municipal solid wastes (MSW) and sewage sludge (SS) via the MixAlco Process. The MSW is an energy source and the SS is a nutrient source for microorganisms.

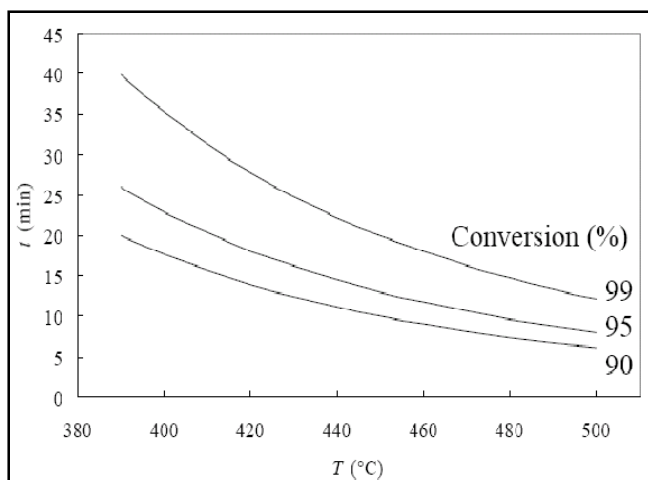


Figure 26 Thermal Conversion Kinetics for MixAlco Process (Granda, 2007)

Transesterification

Transesterification is the reaction of an alcohol with vegetable oil containing triglycerides to produce monoalkyl esters and glycerol (Meher et al., 2006). The glycerol layer settles down at the bottom of the reaction vessel. Diglycerides and monoglycerides are the intermediates in this process. The general reaction for transesterification is shown in Figure 27.

A wide variety of vegetable oils can be used for transesterification. The Table 9 gives a list of oils that can be used with their respective constituent fatty acid content. Linoleic acid and oleic acid are the main constituents for soybean oil. The alcohols that can be used for transesterification depend on the type of esters desired. Methanol (CH_3OH) gives methyl esters and ethanol ($\text{C}_2\text{H}_5\text{OH}$) produces ethyl esters.

Table 9 Fatty Acid Compositions of Common Oils (Meher et al., 2006)

Fatty acid	Soybean	Cottonseed	Palm	Lard	Tallow	Coconut
Lauric	0.1	0.1	0.1	0.1	0.1	46.5
Myristic	0.1	0.7	1	1.4	2.8	19.2
Palmitic	10.2	20.1	42.8	23.6	23.3	9.8
Stearic	3.7	2.6	4.5	14.2	19.4	3
Oleic	22.8	19.2	40.5	44.2	42.4	6.9
Linoleic	53.7	55.2	10.1	10.7	2.9	2.2
Linolenic	8.6	0.6	0.2	0.4	0.9	0

The catalyst used for transesterification may be an acid, a base or a lipase. The commonly used catalysts are given in the Table 10 along with their advantages and disadvantages (Ma et al., 1999, Fukuda et al., 2001, Meher et al., 2006).

The mechanism of alkali-catalyzed transesterification is described in Figure 28. The first step involves the attack of the alkoxide ion to the carbonyl carbon of the triglyceride molecule, which results in the formation of a tetrahedral intermediate. The reaction of this intermediate with an alcohol produces the alkoxide ion in the second step. In the last step the rearrangement of the tetrahedral intermediate gives rise to an ester and a diglyceride.

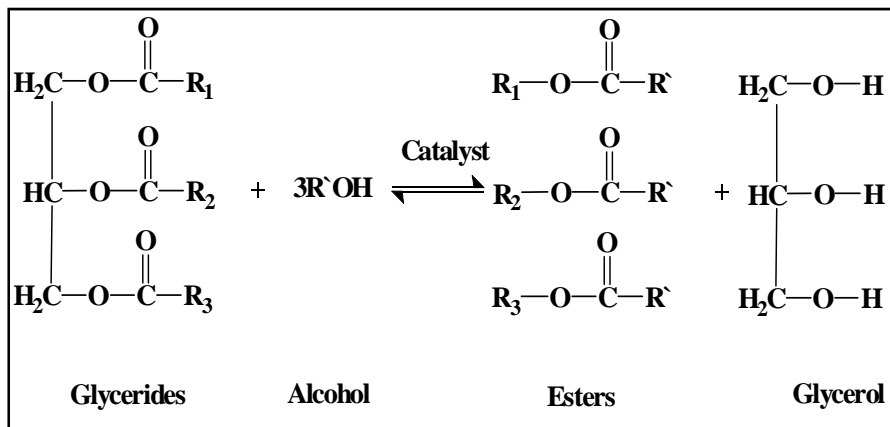


Figure 27 General Transesterification Reaction (Meher et al., 2006)

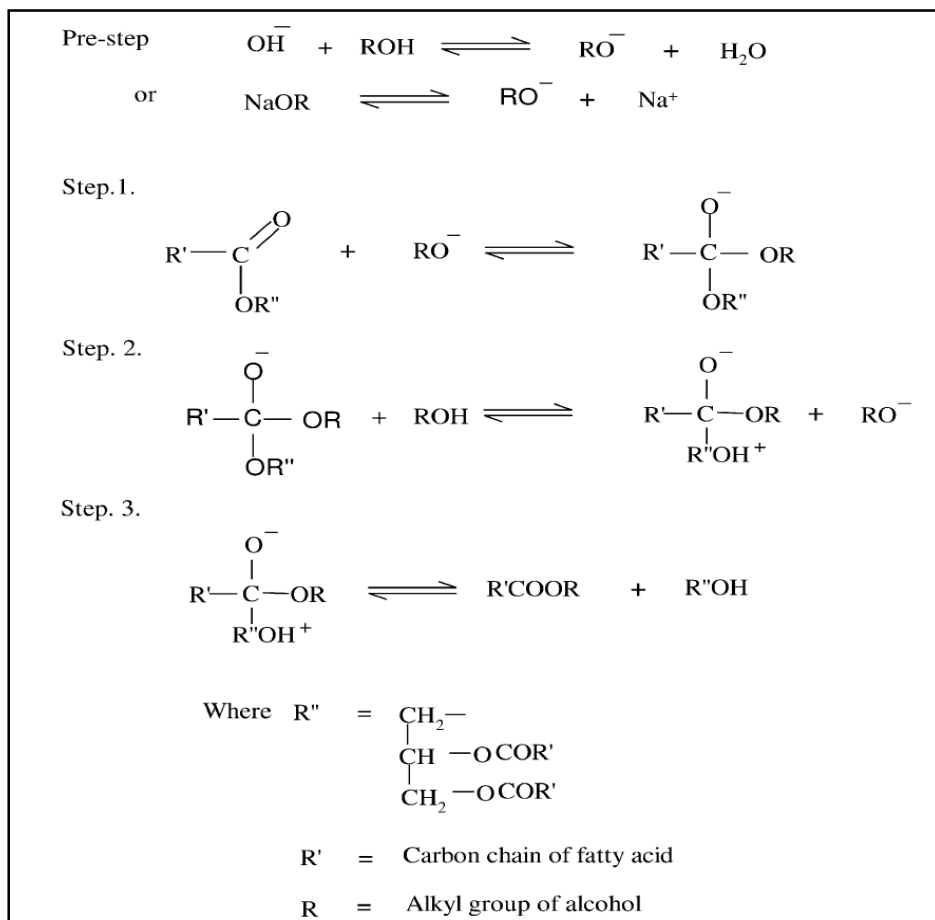


Figure 28 Mechanism of Alkali Catalyzed Transesterification (Meher et al., 2006)

Table 10 Commonly used Catalysts in Transesterification and their Advantages and Disadvantages (Ma et al., 1999, Fukuda et al., 2001, Meher et al., 2006).

Type	Commonly Used compounds/enzymes	Advantages	Disadvantages
Alkali Catalysts	NaOH, KOH, NaOCH ₃ , KOCH ₃ (other alkoxides are also used)	1. Faster than acid catalysed transesterification	1. Ineffective for high free fatty acid content and for high water content (problems of saponification). 2. Energy intensive. 3. Recovery of glycerol difficult. 4. Alkaline waste water requires treatment.
Acid Catalysts	HCl, H ₂ SO ₄ , H ₃ PO ₄ , Sulfonic acid	1. Good for processes with high water content and free fatty acids.	1. Slow process compared to alkali (alkoxides). 2. Require after treatment of triglycerides with alkoxides formed for purification purposes.
Enzyme/lipase/heterogeneous Catalysts	M. miehi, C. antarctica, P. cepacia, C. rugosa, P. fluorescens	1. Possibility of regeneration and reuse of the immobilized residue. 2. Free Fatty Acids can be completely converted to alkyl esters. 3. Higher thermal stability of the enzyme due to the native state. 4. Immobilization of lipase allows dispersed catalyst, reducing catalyst agglomeration. 5. Separation of product and glycerol is easier using this catalyst.	1. Some initial activity can be lost due to volume of the oil molecules. 2. Number of support enzyme is not uniform. 3. Biocatalyst is more expensive than the natural enzyme.

The mechanism of acid catalyzed transesterification of vegetable oil (for a monoglyceride) is shown in Figure 29. It can be extended to di- and tri-glycerides. The protonation of carbonyl group of the ester leads to the carbo-cation, which after a nucleophilic attack of the alcohol produces a tetrahedral intermediate. This intermediate eliminates glycerol to form a new ester and to regenerate the catalyst.

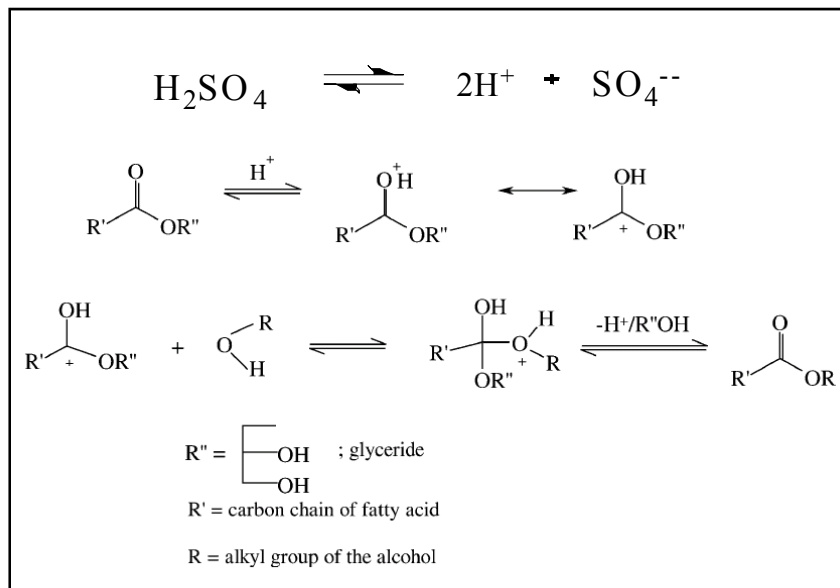


Figure 29 Mechanism of Acid Catalyzed Transesterification (Meher et al., 2006)

Haas et al., 2006 describes a process for the production of methyl esters from the transesterification of soybean oil shown in Figure 30. A two-reactor model was designed with crude degummed soybean oil as feedstock with phospholipid content of less than 50 ppm and negligible fatty acids, sodium methoxide catalyst, and methanol as the alcohol. The design contained three sections, a transesterification section, a purification section and a glycerol recovery section. The transesterification section consisted of two sequential reactors. The purification section has a centrifugation column which separates esters from the aqueous phase. The glycerol recovery and purification section also consists of a centrifugal reactor and subsequent distillation and evaporation columns for an 80% (w/w) glycerol as a byproduct. The cost analysis of the overall process was done with a depreciable life of 10 years and an escalation rate of 1%. Annual production capacity for the methyl ester plant was set at 10×10^6 gallons. With a feedstock cost of \$0.236/lb of soybean oil, a production cost of \$2.00/gallon of methyl ester was achieved.

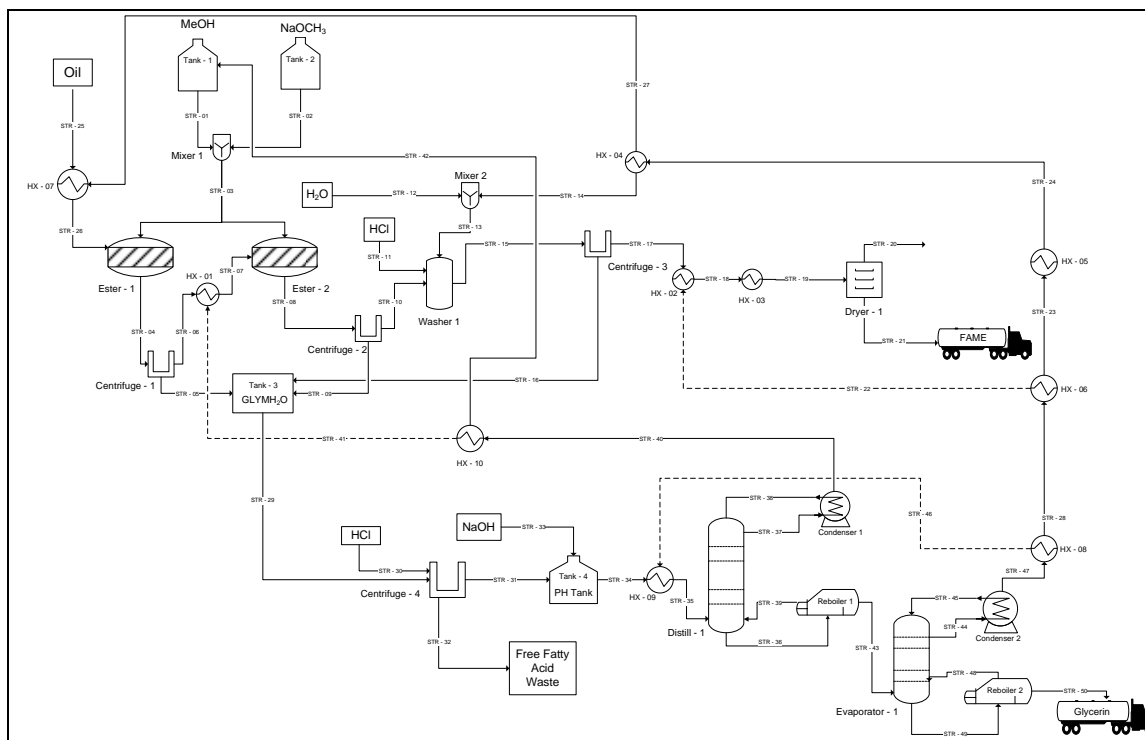


Figure 30 A Process Model for the Production of Fatty Acid Methyl Esters (FAME) and Glycerol

Two vegetable oil processing routes were described by Marinangeli, 2007. As shown in Figure 31, one is for the production of biodiesel and glycerin from transesterification and the other is for the production of green diesel and propane from hydroprocessing. The transesterification route produces mixed fatty acid esters (FAEE and FAME fatty acid ethyl and methyl esters) and glycerin, and the hydroprocessing route produces n-alkanes, propane, carbon dioxide and water. The UOP/Eni Renewable Diesel Process can process vegetable oils in a separate hydrogenation unit to produce green diesel which is combined with the refinery diesel stream, or vegetable oils can be processed with the refinery light cycle oil from the fluid catalytic cracking unit through the refinery hydroprocessing unit (Marinangeli, 2007). Petrobras has a comparable H-Bio process where vegetable oils can also be used directly with petroleum diesel fractions (Costa, 2007).

Of the two routes for vegetable oils, 8.0 % of the product is low value glycerol, but methanol required as a feedstock is only \$10/ton in the transesterification process. The hydrogenation route can process fatty acids in lower cost vegetable oils, but hydrogen required as a feedstock can cost up \$1,000/ton producing an equivalent yield of diesel fuel at \$700/ton (Marinangeli, 2007). At this point neither process has a clear advantage.

Chemical processes of conversion of vegetable oils produces important chemicals that are currently manufactured using petroleum feedstock. Markets that can make use of lipid and vegetable oil based feedstock includes lubricants and hydraulic fluids, solvents, polymers and resins, plasticizers, printing inks, adhesives and surfactants, cosmetics, pharmaceuticals etc.

(Paster et al., 2003). A pathway diagram for these conversions from vegetable oils is given in Figure 32. The main processes involved in the modification of vegetable oils are transesterification and epoxydation. Transesterification is the addition of an alcohol such as methanol or ethanol to break the triglyceride to a glycerol molecule and fatty acids. The fatty acid can then be modified and polymerized using epoxydation or hydroformylation.

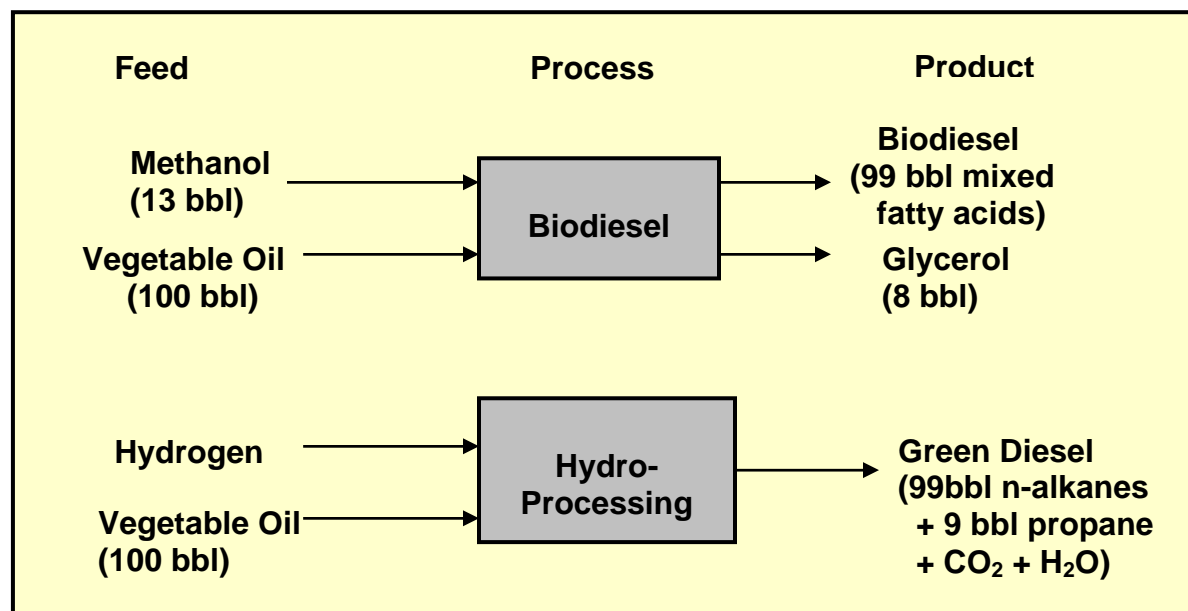


Figure 31 Vegetable Oil Processing Routes (Marinangeli, 2007)

Soybean oil can be used to synthesize polyols, molecules with multiple hydroxyl groups, and these materials can be reacted with isocyanates to produce polyurethanes. Soybean oil can be incorporated into the backbones of unsaturated polyester resins to make composite parts. Soy-based polyols can replace petrochemically derived polyols derived from propylene oxide. Dow and Cargill are bringing soy polyols to market, and the annual market for polyols is 3 billion pounds in the U.S. and 9 billion worldwide. Ford is using soy-based polyurethane foams in automobiles (Tullo, 2007b).

Glycerol is a major byproduct in the transesterification process used to convert the vegetable oils to products. Approximately 10% by weight of glycerol is produced for the transesterification of soybean oil with an alcohol. Cost effective routes to convert glycerin to value-added products are needed. Referring to Figure 33, glycerin can potentially be used in a number of paths for chemicals that are produced and used in the chemical production complex in the lower Mississippi river corridor; the figure is based on information reported by Pellegrino (2000) and Wells (1999).

Glycerin is used now as a general purpose food additive. It has a melting point of 18.2°C, a heat of formation of -582.8 kJ/mol and a free energy of formation of -448.49 kJ/mol at 298 K (Yaws, 1999). It reacts violently with hydrogen peroxide and certain other oxidizers (Sax and Lewis, 1989), and previously only selective oxidation was known to produce glyceric acid and its derivatives. Processes to convert glycerin to intermediates in Figure 33 are being developed, and plants using glycerin as a feed stock could be integrated into the chemical production

complex converting this by-product of biodiesel into products that can displace ones produced now from natural gas. For example, a new low pressure and temperature (200 psi and 200°C) catalytic process for the hydrogenolysis of glycerol to propylene glycol has been reported by Dasari, et al., 2005 that is being commercialized and received the 2006 EPA Green Chemistry Award. Huntsman Corporation plans to commercialize a process for propylene glycol from glycerin, and Ashland, Inc and Cargill have a joint venture underway to produce biobased chemicals in a 65,000 m.t./yr plant in Europe using a new Davy Process Technology glycerin-to-propylene-glycol process (Ondrey, 2007a,b).

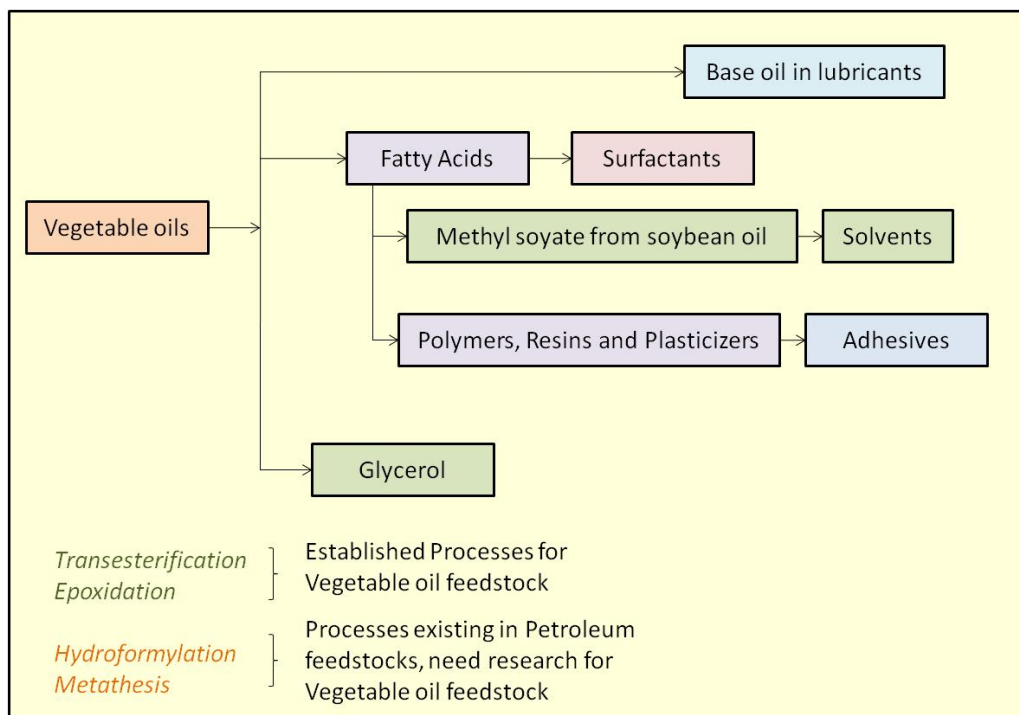


Figure 32 Derivative chains from vegetable oil based feedstock

Both the triglycerides in vegetable oil and methyl esters from the transesterification of vegetable oils can be used as monomers to form resins, foams, thermoplastics and oleic methyl ester (Wool, 2007). A thermosetting polymer is formed by the polymerization of triglycerides with styrene using a free radical initiator and curing for four hours at 100°C. The polymer has very good tensile strength, rigidity and toughness properties. Lignin can enhance toughness, and it can be molded to a material with an excellent ballistic impact resistance. Triglycerides can be functionalized to acrylatedepoxidized soybean oil that can be used for structural foam that has bio-compatibility properties. Methyl esters can be functionalized to epoxidized oleic methyl ester and acrylated oleic methyl ester which can be polymerized with co-monomers methyl methacrylate and butyl acrylate to form oleic methyl ester. A monolithic hurricane-resistant roof has been designed using these materials (Wool, 2007).

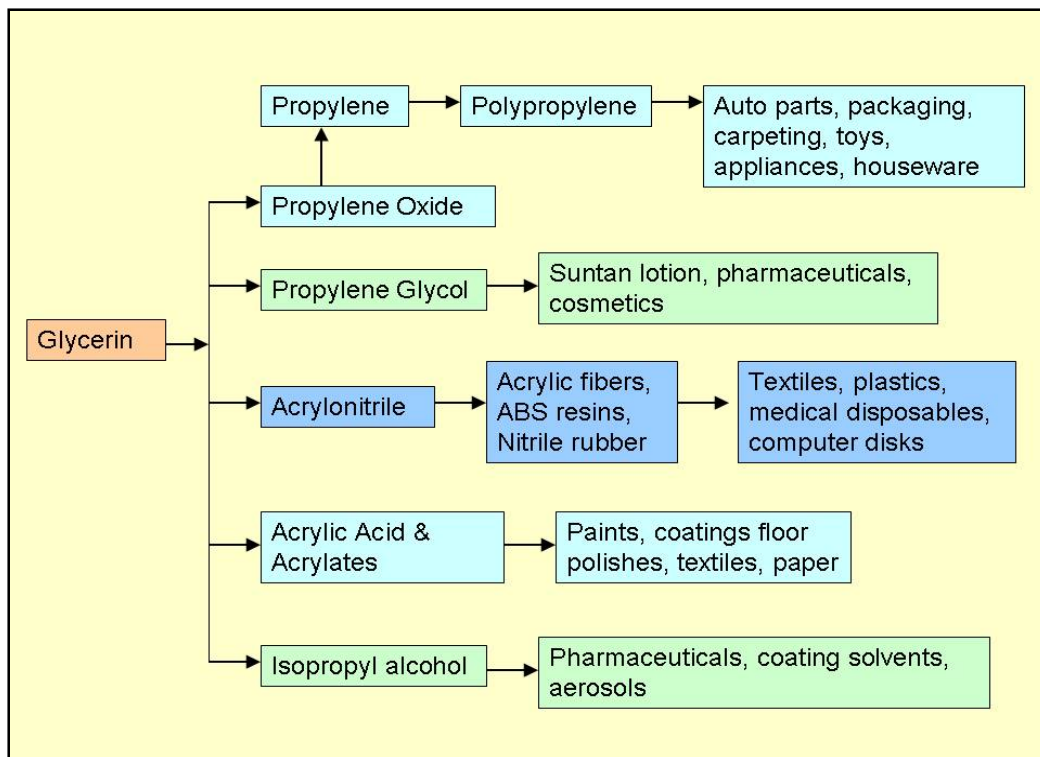


Figure 33 Derivative Chains from Glycerin (Glycerol)

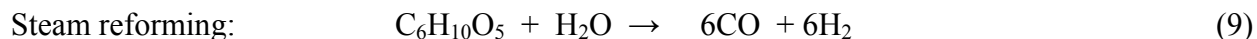
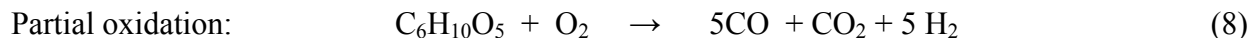
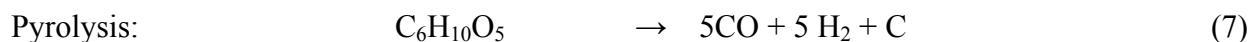
Gasification/Pyrolysis

Thermal conversion such as gasification and pyrolysis can be used to convert biomass to chemicals. Biomass gasification is the conversion of biomass to synthesis gas, a mixture of carbon monoxide and hydrogen. Pyrolysis is the direct thermal decomposition of the organic components in biomass in the absence of oxygen to yield an array of useful products like liquid and solid derivatives and fuel gases (Klass, 1998).

In biomass gasification, steam and oxygen are used to produce synthesis gas where the amount of steam and oxygen are controlled to produce carbon monoxide and hydrogen with a minimum amount of carbon dioxide and other products. Synthesis gas is a 1:1 mixture of carbon monoxide and hydrogen. In the 1800s, coal gasification was used to provide syngas used for lighting and heating (Spath et al., 2003). At the beginning of the 20th century, syngas was used to produce fuels and chemicals. Many of the syngas conversion processes were developed in Germany during the first and second world wars at a time when natural resources were becoming scarce for the country and alternative routes for hydrogen production, ammonia synthesis, and transportation fuels were a necessity. With the development of the petroleum industry in the 1940s and beyond, the economics of many of the old syngas routes became unfavorable and those processes were replaced by petroleum-based processes. Now, the United States is facing a similar crisis with rising prices of crude petroleum and natural gas, and alternative ways of using biomass as a feedstock are being analyzed. Coal co-fired with biomass and complete biomass gasification processes are alternatives that are being considered for the production of syngas for fuels and chemicals. Biomass gasification technologies are similar to coal gasification and both

produce similar product gases. However, since biomass contains more volatile matter, gasification occurs at lower temperatures and pressures than coal, and pyrolytic chars are more reactive than coal products. The increase in pressure lowers equilibrium concentrations for hydrogen and carbon monoxide and increases the carbon dioxide and methane concentrations. Biomass contains oxygen in cellulose and hemicellulose, and that makes them more reactive than oxygen-deficient coal. Volatile matter in biomass is about 70-90% in wood vs 30-45% in coal.

Commercial biomass gasification facilities started worldwide in the 1970's and 1980's. Typically, gasification reactors comprise of a vertical reactor that has drying, pyrolysis and combustion zones. Synthesis gas leaves the top of the reactor and molten slag leaves the bottom of the reactor. The reactions that take place in the reactor are given in Equation 7, 8 and 9 using cellulose as representative of biomass (Klass, 1998).



Synthesis gas is used in the chemical production complex of the lower Mississippi River corridor to produce ammonia and methanol. Currently, ammonia and methanol are produced using synthesis gas from natural gas, naphtha or refinery light gas. Nearly 12.2 billion pounds of methanol are produced annually in the USA and most of the methanol is converted to higher value chemicals such as formaldehyde (37%), methyl tertiary butyl ether (28%) and acetic acid (8%) (Paster, 2003). Ethanol can be produced from the synthetic gas, and Fischer-Tropsch chemistry is another approach to convert synthesis gas to chemicals and fuels. The chemicals that can be produced include paraffins, monoolefins, aromatics, aldehydes, ketones, and fatty acids.

Pyrolysis is the direct thermal decomposition of the organic components in biomass in the absence of oxygen to yield an array of useful products like liquid and solid derivatives and fuel gases (Klass, 1998). Conventional pyrolysis is the slow, irreversible, thermal degradation of the organic components in biomass in absence of oxygen and includes processes like carbonization, destructive distillation, dry distillation and retorting. The products of pyrolysis under high pressure and temperature include mainly liquids with some gases and solids (water, carbon oxides, hydrogen, charcoal, organic compounds, tars and polymers). The pyroligneous oil is the liquid product formed and mainly composed of water, settled tar, soluble tar, volatile acids, alcohols, aldehydes, esters and ketones. Depending on pyrolysis conditions and feedstock, the liquid product contains valuable chemicals and intermediates. The separation of these intermediates in a cost effective manner is essential.

Dow Chemical Company and National Renewable Energy Laboratory have a combined process using NREL's expertise in biomass gasification and Dow's catalytic process to convert biomass into mixed alcohols from syngas (Ondrey, 2008). The process can use agricultural and forestry waste and energy crops as feedstock. The waste biomass is pelletized and gasified with steam in a fluidized bed at 675-750 °C to produce syngas. The syngas is then converted into

mixed alcohols using molybdenum sulfide-based catalyst developed by Dow. The conversion takes place in a gas-phase tubular reactor at about 300°C and 1500 psi (or higher) and yields a mixture of ethanol (main component), propanol, methanol and small amounts of other higher alcohols. The catalyst will be tested in a 0.5 ton/day pilot gasification plant. The energy balance ratio (energy yielded over energy needed for production) for cellulosic ethanol is 6:1 compared to 1.3:1 for corn ethanol.

ConocoPhillips has funded a \$22.5 million and 8 year research program at Iowa State University to develop new technologies for processing lignocellulosic biomass to biofuels (C&E News, 2007a). The company wants to investigate routes using fast pyrolysis to decompose biomass to liquid fuels.

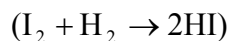
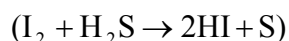
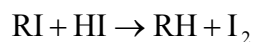
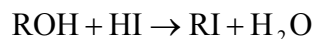
Faustina Hydrogen Products LLC announced a \$1.6 billion gasification plant in Donaldsonville, Louisiana to begin operation in 2010 (McMillan, 2007a). The plant will use petroleum coke and high sulfur coal as feedstocks instead of natural gas to produce anhydrous ammonia for agriculture, methanol, sulfur and industrial grade carbon dioxide. Capacities of the plant include 4,000 tons per day of ammonia, 1,600 tons per day of methanol, 450 tons per day of sulfur and 16,000 tons per day of carbon dioxide. Mosaic Fertilizer and Agrium Inc. have agreements to purchase the anhydrous ammonia from the plant. The carbon dioxide will be sold to Denbury Resources Inc. for use in enhanced oil recovery of oil left after conventional rig drilling processes in old oil fields in Southern Louisiana and the Gulf Coast. The rest of the carbon dioxide would be sequestered or sold as an industrial feedstock. The facility claims to have the technology to capture all the carbon dioxide during manufacturing process.

Eastman Chemical Company, a Fortune 500 company, will provide the Faustina gasification plant with necessary maintenance and services and plans to have a 25% equity position along with a purchase contract to buy the methanol produced in the plant (McMillan, 2007b). Eastman Chemicals will use methanol to make raw materials like propylene and ethylene oxide (Tullo, 2007a). Faustina is also backed by D. E. Shaw Group and Goldman Sachs.

Eastman Chemicals also plans to have 50% stake in a \$1.6 billion plant to be built in Beaumont, Texas in 2011 (Tullo, 2007a). The plant will use gasification of petroleum coke to produce syngas. Eastman will use the syngas to produce 225 million gallons of methanol and 225,000 metric tons of ammonia per year at Terra Industries in Beaumont. Air Products & Chemicals will supply 2.6 million metric tons per year of oxygen to the gasifiers and market the hydrogen produced in the complex.

Thermal liquefaction is the direct thermal conversion of biomass to liquid fuels using a liquid medium (Klass, 1998). The liquid medium can be aqueous or non-aqueous (hydriodic acid, alkaline compounds like sodium carbonate etc.). Reduction of biomass with hydriodic acid (HI) is considered the most innovative way to convert biomass into chemicals. This process is carried out at low temperature and low pressure to yield liquid hydrocarbons. A 57 wt% aqueous hydroiodic acid forms an azeotrope at 127°C. The cellulose in biomass is treated with the azeotrope at 127°C and a stoichiometric excess of 1.6 -3.8 times of HI. The cellulose, under these conditions, is rapidly hydrolyzed to hydrocarbon-like molecules. The yields are 60-70% with

reaction times of 0.5 min. The hydriodic acid regeneration can be carried out with hydrogen sulfide, as shown in the reaction scheme below.



In summary, gasification has a long history of development and use. Coal distillation was performed in 1792 and used for London lighting in 1802. Menthol alcohol was produced by BASF by Fischer Tropsch in the 1920s, and SASOL began operation in 1955. Current pathways include low and high pressure gasification, and low pressure indirect gasification (Bain, 2007).

Biomass Conversion Products – by Carbon Number

Biomass can be converted to chemicals using the routes described in the previous section. The Biomass Research and Development Act of 2000 had set up a Biomass R&D Technical Advisory Committee which has fixed a goal of supplying USA with 25 percent of its chemicals from biomass by the year 2030 (Perlack, 2005). Bulk chemicals can be defined as those costing \$1.00 - \$4.00 per kg and produced worldwide in volumes of more than one million metric tons per year (Short, 2007). The production cost of these chemicals can be reduced by 30% when petrochemical processes are replaced by biobased processes. Some of these chemicals are discussed in the following sections.

Single-Carbon Compounds

Methane: Methane from natural gas is an important industrial raw material for the production of acetylene, synthesis gas, methanol, carbon black etc (Austin, 1984). Natural gas is a non-renewable source, and ways to produce methane from biomass are needed.

An innovative process using pyrolytic gasification for methane production from biomass is given by Klass, 1998 and shown in Figure 34. Biomass is fed to the pyrolysis reactor operating at 800°C. The reactor temperature is maintained at this temperature by sand fed from the combustion reactor at 950 °C. The biomass decomposes into pyrolysis gas (~40% CO, ~30% H₂ and others) which exits from the top of the reactor. Char is deposited on the sand which is sent to the combustion reactor, and air is fed to this reactor to maintain the temperature at 950 °C from combustion of the char. The pyrolysis gas can then be sent to a methanation reactor as shown in Figure 34.

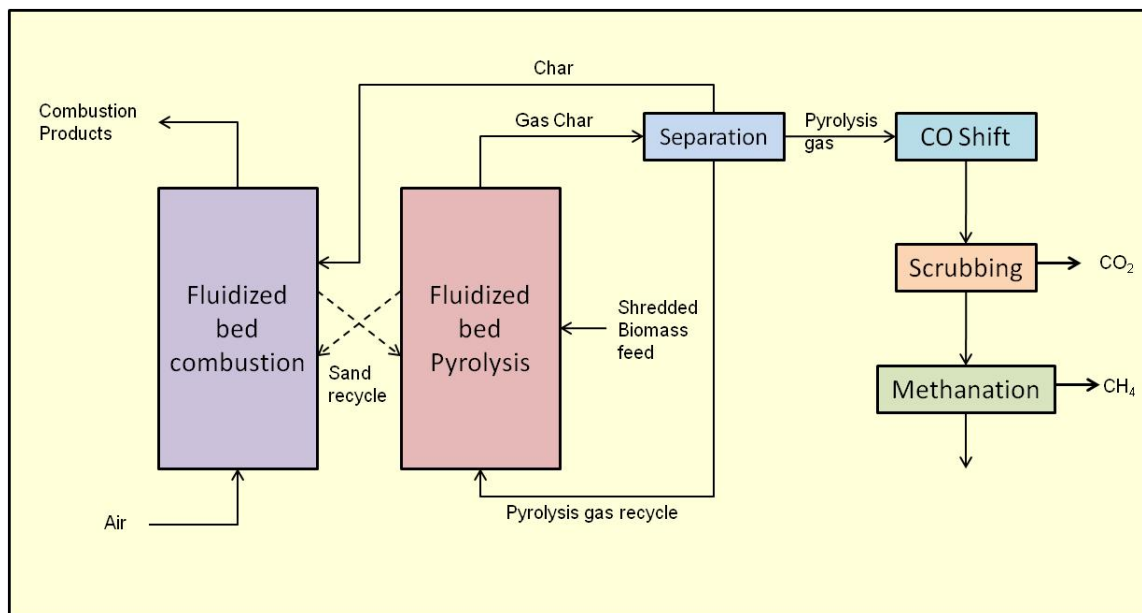


Figure 34 Pyrolytic Gasification Process Using Two Fluidized Bed Reactors (Klass, 1998).

Methanol: Methanol was historically produced by the destructive distillation of wood (Wells, 1999). Currently, 97% of methanol production is based on natural gas, naphtha or refinery light gas. Large scale methanol manufacture processes based on hydrogen-carbon oxide mixtures were introduced in the 1920s. In the 1970s, low pressure processes replaced high pressure routes for the product formation. Currently, methanol is produced using adiabatic route of ICI and isothermal route of Lurgi. Capacities of methanol plants range from 60,000 to 2,250,000 tons per year. Nearly 12.2 billion pounds of methanol are produced annually in the USA and around 85% of it is converted to higher value chemicals such as formaldehyde (37%), methyl tertiary butyl ether (28%) and acetic acid (8%) (Paster, 2003).

The chemical production complex in the lower Mississippi River corridor produces methanol from natural gas and carbon dioxide produced from ammonia plant. As ammonia plants are shut down due to rising natural gas prices, alternate methods for the production of methanol are needed. New processes for producing methanol in the chemical production complex using CO₂ as a feedstock are given by Xu, 2004. If large-scale carbon nanotube processes in the order of 5000 metric tons per year are integrated into the complex (Agboola, 2005), comparable amounts of CO₂ will be produced which can compensate for the carbon dioxide from the shut down ammonia plants.

Two-Carbon Compounds

Ethanol: Ethanol has been produced by fermentation of carbohydrates for many thousands of years (Wells, 1999). Economic, industrial manufacture of ethanol began in the 1930's. Current processes to produce ethanol in the industry include direct and indirect hydration of ethylene and carbonylation of methyl alcohol and methyl acetate. However, increasing prices of crude petroleum has prompted the research for manufacture of ethanol from biomass sources. Ethanol can be produced by the fermentation of starch (corn) sugar (sugarcane) or waste

lignocellulosic biomass like corn stover or switch grass. The processes for conversion depend on the feedstock used. The reaction for fermentation of glucose to ethanol is given by Equation 6. Capacities of ethanol plants range from 5000 to 210,000 tonnes per year. Marathon Oil has joined Andersons, an Ohio based grain producer, to build and operate ethanol plants, with an initial facility having an annual capacity of 110 million gallons (C&E News, 2006). Celunol is operating the first U. S. cellulosic ethanol pilot plant in Jennings, LA using bagasse and is completing a 1.4 million gallon per year demonstration facility. Celunol's technology has been licensed to Marubeni Corporation (Tokyo, Japan) which operates a 1.4 million liters per year cellulosic ethanol plant using wood waste (McCoy, 2007).

Industrial uses of ethanol include use as solvents and in the synthesis of chemicals (Wells, 1999). 45% of total ethanol demand is for solvent applications. Ethanol is a chemical intermediate for the manufacture of esters, glycol ethers, acetic acid, acetaldehyde and ethyl chloride and this demand as intermediate accounts for 35% of its production. Ethanol can also be converted to ethylene and that serves as a raw material for a wide range of chemicals that are presently produced from petroleum-based feedstock.

Ethanol can be produced from sugars (glucose), starch and cellulose. Sugars can be directly converted to ethanol using *S.cerevisiae* without any pretreatment (Klass, 1998). For starch-containing grain feedstock, the cell walls must be disrupted to expose the starch polymers so that they can be hydrolyzed to free, fermentable sugars as yeast does not ferment polymers. The sugar polymers in grain starches contain about 10-20% hot-water-soluble amylases and 80-90% water-insoluble amylopectins. Both substances yield glucose or maltose on hydrolysis. Cellulosic or lignocellulosic biomass is mainly composed of crystalline and amorphous cellulose, amorphous hemicelluloses, and lignin as binder. The main problems associated with using this feedstock lie in the difficulty of hydrolyzing celluloses to maximize glucose yields and the inability of yeasts to ferment the pentose sugars which are the building blocks of the hemicelluloses.

The standard biochemical process for ethanol production from starch, e.g., corn, is shown in Figure 35. In this wet milling process, corn is milled to disrupt the cell walls and expose the starch. The material is "cooked" with steam to solubilize and partially hydrolyze the starch to glucose using amylase at 93°C. Hydrolysis to glucose is completed using glucoamylase at about 65°C (Klass, 1998, Atkinson and Mavituna, 1983). Then glucose is converted to ethanol and carbon dioxide in the fermenter with a 90% yield by the reaction $C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2$ at about 30°C with a residence time of about 40 hours. After removing the nonfermentable solids (slop), the liquid is sent to distillation columns to concentrate the ethanol to 95% alcohol (an azeotrope). Concentrating to pure alcohol can be done in an azeotropic distillation column with benzene or by reaction of water with calcium oxide and further distillation (Speight, 2002).

There are three other processes that are used to convert corn to products. The alkaline process is used for corn chips and tortillas. The dry milling process is used for corn meal and breakfast cereals. The dry-grinding process is used for potable ethanol and fuel ethanol (Cheryan, 2007).

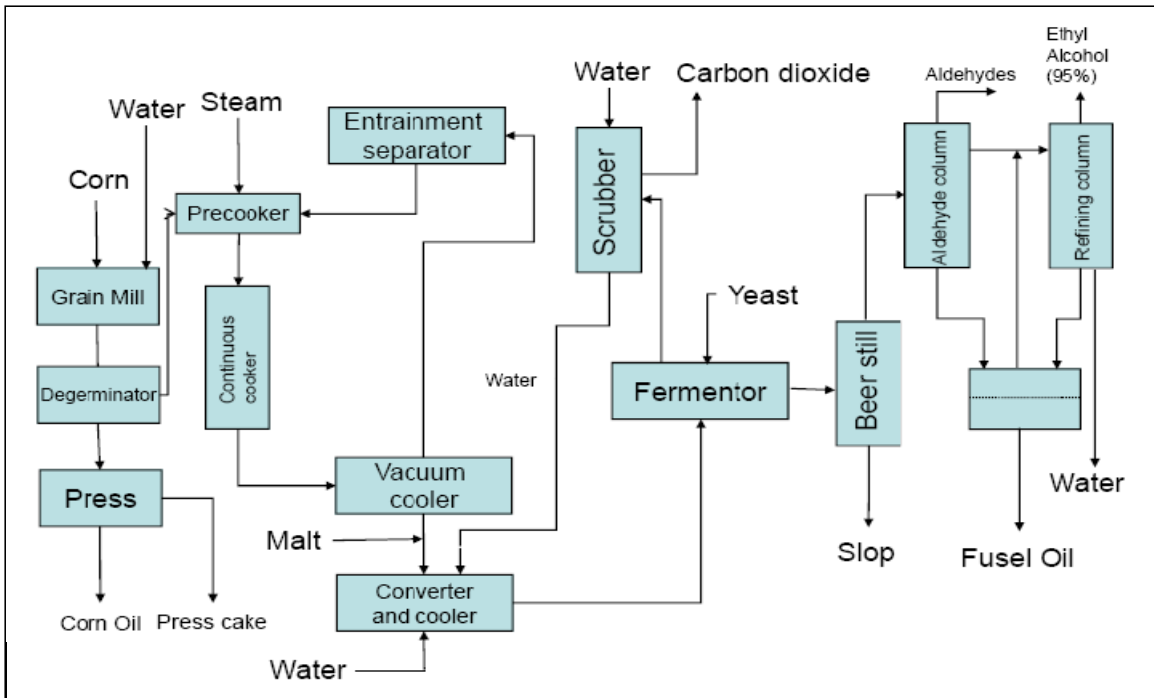


Figure 35 Wet Milling Process using Corn to Produce Ethanol (Klass, 1998)

Currently, 60% of the world's biobased ethanol is obtained from sugar cane in Brazil. Sugar from sugar cane is used directly as a solution from the grinding of the cane and it is sent directly to fermenters rather than proceeding with clarification, evaporation and crystallization to produce raw sugar that is sent to a sugar refinery. An ethanol plant in Brazil is shown in Figure 36 that requires no additional energy. Power and steam are generated by burning bagasse. The other photograph shows a vast sugar cane field in Brazil (Borne, 2007). Sorghum is the feedstock for about 3 percent of U.S. ethanol production. Other feedstocks include molasses, cassava, rice, beets and potatoes.

The production of ethanol reached 5.0 billion gallons in 2006 and consumed 20% of the U.S. corn crop (Johnson, 2007b). The annual capacity of ethanol from corn increased by 2.2 billion gallons from 2005 values to a total of 6.7 billion gallons produced annually (Hess, 2006b). If this trend and the existing and anticipated policy incentives in support of ethanol continue, U.S. ethanol production could reach 7 billion gallons in 2010, 3.3 billion gallons more than the amount produced in 2005 (ERS/USDA, 2006).

In the processes using sugar and cellulose, carbon dioxide is an emission. Other emissions include volatile organic compounds, nitrogen oxides, particulates and others in regulated pollutants. The Environmental Protection Agency changed the Federal regulations for new ethanol plants to 250 tons per year from the previous threshold of 100 tons per year (Johnson, 2007).



Figure 36 Plant in Brazil Producing Ethanol from Sugar Cane and Vast Sugar Cane Field (Borne, 2007).

Cellulosic biomass refers to a wide variety of plentiful materials obtained from plants, including certain forest-related resources (mill residues, pre-commercial thinning, slash, and brush), many types of solid wood waste materials, and certain agricultural wastes (including corn stover), as well as plants that are specifically grown as fuel for generating electricity. These materials can be used to produce ethanol which is referred to as “cellulosic ethanol.” A block diagram for producing ethanol from cellulosic biomass, bagasse in this case, is shown in Figure 37.

Six plants were selected by DOE to receive federal funding for cellulosic ethanol production (DOE, 2007). These plants received a sum of \$385 million for biorefinery projects which will produce more than 130 million gallons of cellulosic ethanol per year. Table 11 gives a list of these plants with their capacities for producing ethanol. The BCI process for the conversion of sugarcane bagasse to ethanol is shown in Figure 37.

Ondrey, 2008 reports the production of ethanol for less than \$1 per gallon using a process developed by ZeaChem, Inc.. The company has a pilot process and plans to startup a 1.5 million-gallon/year demonstration plant at the end of 2009. The process uses acid hydrolysis of biomass to obtain sugars. Then, instead of fermentation with yeast, acetogen bacteria (found in termites) is used to obtain acetic acid. The acid is then converted to an ester, like ethyl ester. The lignin from the process is gasified to produce hydrogen and this hydrogen is used to hydrogenate the ethyl ester to ethanol. The process can produce 160 gallons of ethanol per ton of biomass, a 50% increase from standard ethanol production.

Table 11 DOE Funded Cellulosic Ethanol Plants (DOE, 2007)

Plant Name/ Location/ Startup Year	Feedstock	Feedstock Capacity (tons/day)	Products	Notes
Abengoa Bioenergy Biomass of Kansas LLC Colwich, Kansas, 2011	Corn Stover, Wheat straw, Sorghum stubble, Switchgrass	700	Ethanol: 11.4 million gallons/year Syngas	Thermochemical and Biochemical processing
ALICO, Inc. LaBelle, Florida, 2010	Yard, Wood, Vegetative wastes (citrus peel)	770	Ethanol: 7 million gallons/year (first unit) 13.9 million gallons/year (second unit) Power: 6,255 KW Hydrogen Ammonia	Gasification Fermentation of syngas to ethanol
BlueFire Ethanol, Inc. Southern California, 2009	Sorted green waste and wood waste from landfills	700	Ethanol: 19 million gallons/year	Concentrated acid processing Fermentation
Broin Companies Emmetsburg, Palo Alto County, Iowa, 2010	Corn fiber, Corn stover	842	Ethanol: 125 million gallons/year Chemicals Animal feed	Fermentation of starch and lignocellulosic biomass (25%)
Iogen Biorefinery Partners, LLC Shelley, Idaho, 2010	Agricultural residues: wheat straw, barley straw, corn stover, switchgrass and rice straw	700	Ethanol: 18 million gallons/year (first plant) 250 million gallons/year (future plants)	Enzymatic process converting cellulose to ethanol
Range Fuels, Inc. Near Soperton, Treutlen County, Georgia 2011	Unmerchantable timber and forest residues	1200	Ethanol: 10 million gallons/year (first unit) ~40 million gallons/year (commercial unit) Methanol: 9 million gallons/year (commercial unit)	Thermochemical Catalytic syngas conversion

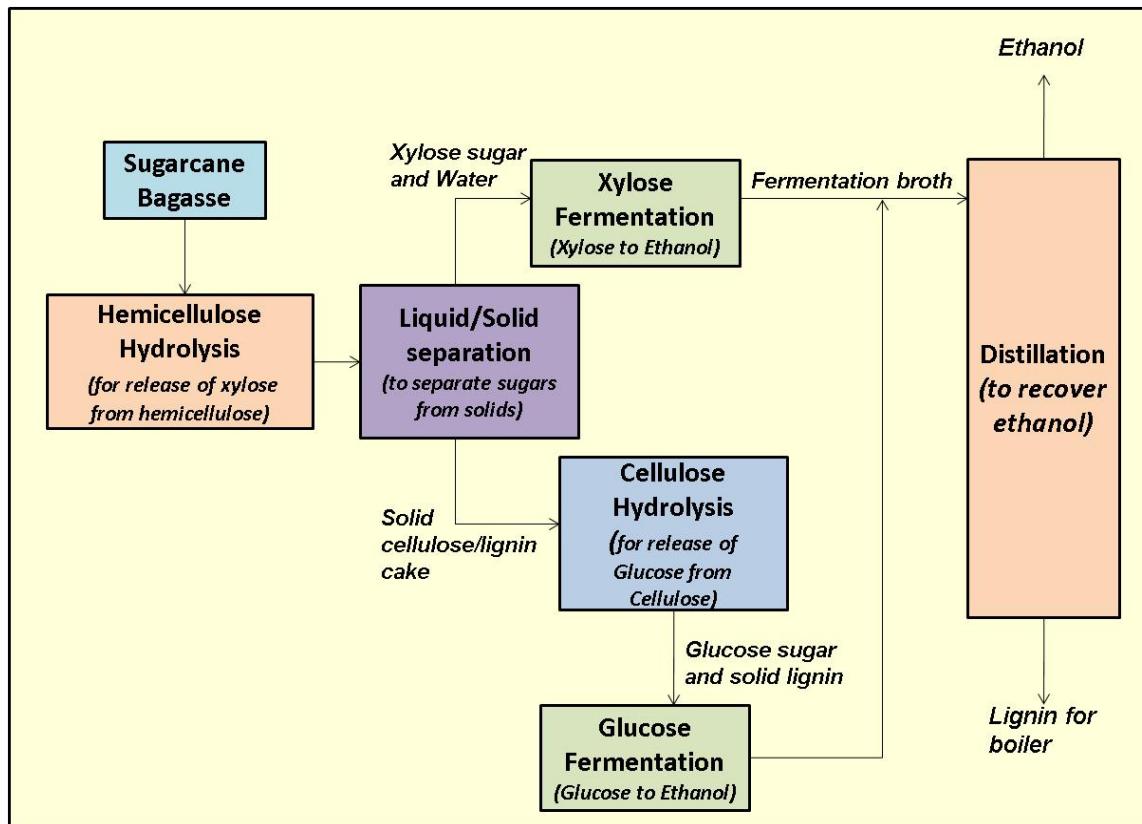


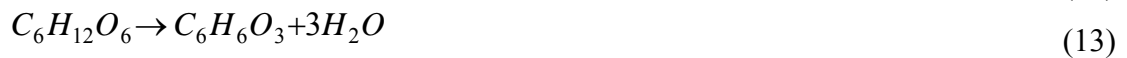
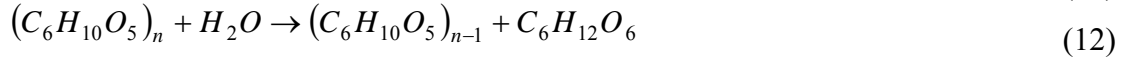
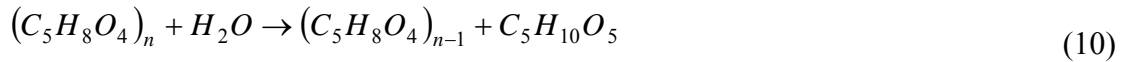
Figure 37 BCI Process for Converting Sugarcane Bagasse to Ethanol (Smith, 2005)

Tolan, 2006 describes the Iogen's process for production of ethanol from cellulosic biomass. Iogen is one of the six companies of Table 11 that were identified by DOE to receive federal funding to produce ethanol from lignocellulosic feedstock. The facility produces 2000 gallons/day of ethanol from wheat straw in a pilot plant, with proposal to scale up to 170,000 gallons/day (60 million gallons/year). The wheat straw is also mixed with corn stover or other grass and pretreated using acid hydrolysis. Cellulose hydrolysis is then carried out with cellulase enzymes added to break the cellulose into glucose. The cellulase enzymes are prepared in a plant site using a wood-rotting fungus in large fermentation vessels. The cellulose hydrolysis is followed by sugar separation and fermentation using recombinant *Saccharomyces* yeast capable of fermenting both glucose and xylose. The residual cellulose and lignin in the biomass is removed and burned for energy. The ethanol is removed using conventional distillation. The feedstock selection depended on the following considerations:

- Low cost: Desired feedstock should be available and delivered to plant at low cost. Primary and secondary tree growth, sawdust and waste paper have existing markets and were not considered for the process.
- Availability: Feedstock availability should be consistent and in the order of 800,000 tons/year which is not generally available from sugarcane bagasse.
- Uniformity: Feedstock available should be consistent and hence municipal waste containing foreign matter is not considered.

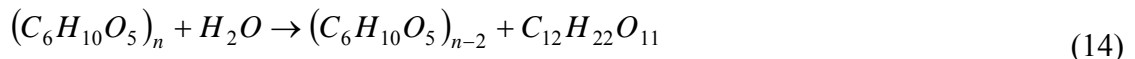
- Cleanliness: High levels of silica can cause damage to equipment. Microbial contamination and toxic or inhibitory products should be kept out of the feedstock.
- High potential ethanol yield: Cellulose and hemicellulose should be present in high percentage in the feed to yield maximum ethanol by fermentation. Wood and forestry waste has high lignin content which inhibits fermentation.
- High efficiency of conversion: The efficiency of conversion in the Iogen process depended on arabinan and xylan content in feedstock. These are constituent hemicelluloses and low content of these required high quantities of enzyme for conversion to cellulose, thereby increasing the process cost.

The Iogen process uses steam explosion pretreatment for chopped, milled wheat straw. High pressure steam and 0.5-2% sulfuric acid are added to the feedstock at a temperature of 180-260°C. The residence time in the pretreatment reactor is 0.5-5 minutes. The pressure is released rapidly to enable the steam explosion process. Hemicellulose reacts first in the process according to Equation 2-10. The dilute sulfuric acid produces xylose monomer, which dehydrates to furfural according to Equation 2-11 under further pretreatment conditions. Similar reactions occur for arabinose. Small amounts of cellulose react to glucose by Equation 2-12 and further degrade to hydroxymethylfurfural according to Equation 2-13. The lignin depolymerizes in this process but is insoluble in the acid or water.



The next step is the preparation of cellulase enzymes. In the Iogen process, *Trichoderma*, a wood rotting fungus is used to produce cellulase enzymes. The cellulases are prepared in submerged liquid cultures in fermentation vessels of 50,000 gallons. The liquid broth contains carbon source, salts, complex nutrients like corn steep liquor and water. The carbon source is important and includes an inducing sugar (like cellobiose, lactose, sophorose and other low molecular weight oligomers of glucose) promoting cellulase growth as opposed to glucose which promotes growth of the organism. The nutrient broth is sterilized by heating with steam. The fermenter is inoculated with the enzyme production strain once the liquid broth cools down. The operating conditions of the fermenter are 30°C at a pH 4-5. The temperature is maintained using cooling coils of water, and pH is maintained using alkali. Constant stream of air or oxygen is passed to maintain aerobic conditions required for *Trichoderma*. The cellulase enzyme production process requires about one week and at the end of the run, is filtered across a cloth to remove cells. The spent cell mass is disposed in landfills. Cellulase enzymes can be directly used at Iogen's ethanol manufacturing facility. The enzymes can also be stored provided they are sterilized against microbial contamination by using sodium benzoate and protein denaturation by using glycerol. Iogen reduces the cost of their ethanol manufacture by having an onsite cellulase manufacture facility, reducing costs due to storage and transportation of enzymes.

The cellulase enzymes are conveyed to hydrolysis tanks to convert cellulose to glucose. The slurry from pretreatment containing 5-15% total solids is fed into hydrolysis tanks having a volume of 200,000 gallons. Crude cellulase enzymes broth is added in dosages of 100 liters/ton of cellulose. The contents are agitated to keep material dispersed in the tank. The hydrolysis proceeds for 5-7 days. The viscosity of the slurry decreases and lignin remains as insoluble particles. The cellulose hydrolysis process yields 90-98% conversion of cellulose to glucose. Enzymatic hydrolysis of cellulose occurs according to Equations 14 and 15.



The hydrolysis slurry is separated from lignin and unreacted cellulose using a plate and frame filter. The filter plates are washed with water to ensure high sugar recovery. The sugar stream is pumped to fermentation tanks. The lignin cakes can be used for power generation by combustion and excess electricity can be sold to neighboring plants. The sugar stream is fermented with genetically modified *Saccharomyces* yeast capable of fermenting both glucose and xylose. The yeast is well developed for plant operations with good ethanol tolerance. The rates and yields of xylose fermentation are not high in the current process leaving scope for further improvement. The fermentation broth obtained after fermentation is pumped into a distillation column. Ethanol is distilled out at the top and dehydrated. Yield of ethanol obtained in the process is 75 gallons/ton of wheat straw.

Aden et al., 2002 described the use of lignocellulosic biomass for the production of ethanol from corn stover. Plant size was 2000 metric tons/day corn stover, and the design of the facility was divided into 8 sections (A100-A800) as shown in the Figure 38. The cost estimate is based on the assumption that the plant developed is an “nth” plant of several plants that are already built using same technology and are operating. The target selling price of ethanol is \$1.07 per gallon with a startup date for plant in 2010. The conceptual design for this plant includes equipment design, corn stover handling, and purchase of enzymes from commercial facilities like Genecor International and Novozymes Biotech. The design did not take into account the sale of byproducts which are important commodity and specialty chemicals.

The feedstock, in this case corn stover (comprised of stalks, leaves, cobs, and husks), is delivered to the feed handling area (A100) for storage and size reduction. From there the biomass is conveyed to pretreatment and detoxification (A200). In this area, the biomass is treated with dilute sulfuric acid catalyst at a high temperature for a short time, liberating the hemicellulose sugars and other compounds. Separation with washing removes the acid from the solids for neutralization. Overliming is required to remove compounds liberated in the pretreatment that are toxic to the fermenting organism. Detoxification is applied only to the liquid portion of the hydrolysis stream.

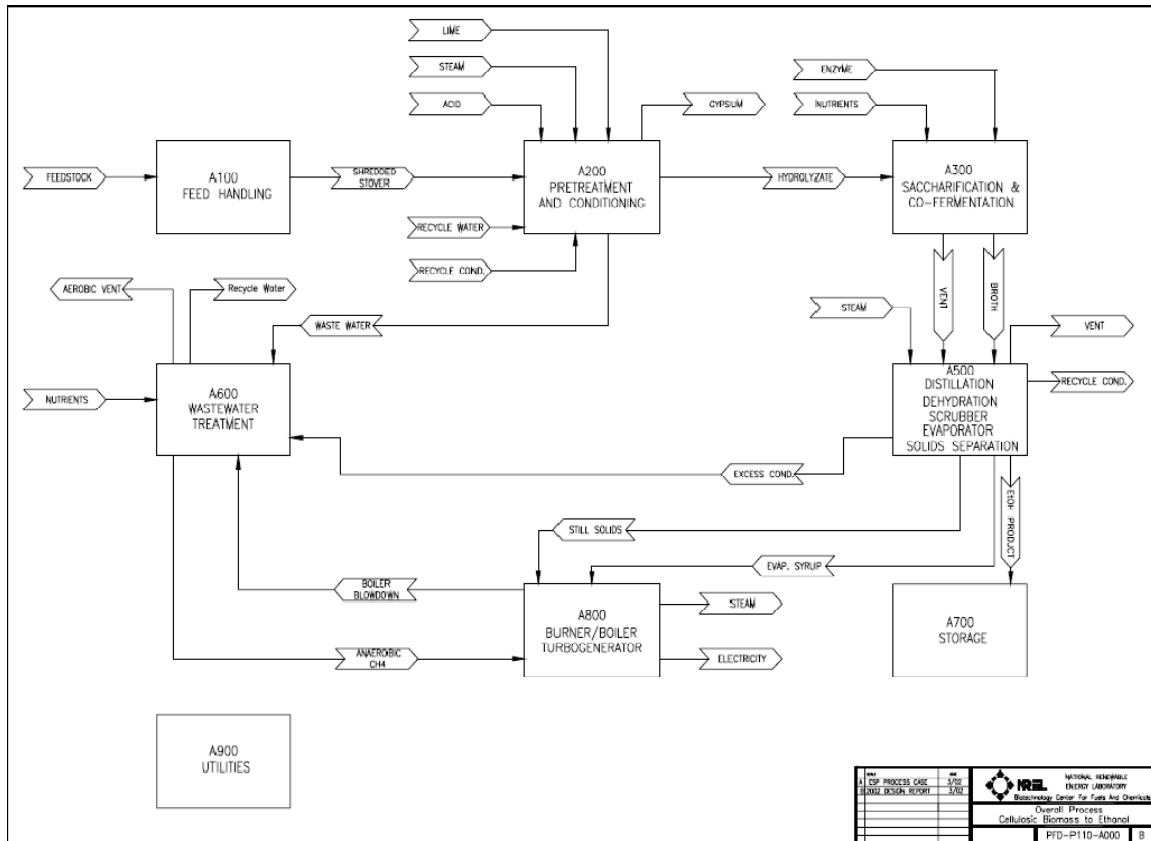


Figure 38 Design for the Production of Ethanol from Corn Stover (Aden et al., 2002)

Enzymatic hydrolysis (or saccharification) coupled with co-fermentation (A300) of the detoxified hydrolyzate slurry is carried out in continuous hydrolysis tanks and anaerobic fermentation tanks in series. A purchased cellulase enzyme preparation is added to the hydrolyzate in the hydrolysis tanks that are maintained at a temperature to optimize the enzyme's activity. The fermenting organism, *Zymomonas mobilis*, is first grown in a series of progressively larger batch anaerobic fermentations to make enough cells to inoculate the main fermenters. The inoculum, along with other nutrients, is added to the first ethanol fermenter along with the partially saccharified slurry at a reduced temperature. The cellulose will continue to be hydrolyzed, although at a slower rate, at the lower temperature. After several days of separate and combined saccharification and co-fermentation, most of the cellulose and xylose are converted to ethanol. The resulting beer is sent to product recovery.

Product recovery (A500) involves distilling the beer to separate the ethanol from the water and residual solids. A mixture of nearly azeotropic water and ethanol is dehydrated to pure ethanol using vapor-phase molecular sieve. Solids from the distillation bottoms are separated and sent to the boiler. Concentration of the distillation bottoms liquid is performed by evaporation, using waste heat. The evaporated condensate is returned to the process and the concentrated syrup is sent to the combustor.

Part of the evaporator condensate, along with other wastewater, is treated by anaerobic and aerobic digestion (A600). The biogas (high in methane) from anaerobic digestion is sent to

the combustor for energy recovery. The treated water is suitable for recycling and is returned to the process.

The solids from distillation, the concentrated syrup from the evaporator, and biogas from anaerobic digestion are combusted in a fluidized bed combustor (A800) to produce high-pressure steam for electricity production and process heat (Aden et al., 2002). The majority of the process steam demand is in the pretreatment reactor and distillation areas. Generally, the process produces excess steam that is converted to electricity for use in the plant and for sale to the grid. The plant size for design in the NREL report (Aden et al., 2002) was set at an optimum between 2000 and 4000 m.t./day. This size was considered on the basis of certain factors described below.

Economies of Scale: The plant size varies with capital cost according to the Equation 16. If exponential, exp , equals 1, linear scaling of plant size occurs. However, if the exponential value is less than 1, then the capital cost per unit size decreases as the equipment becomes larger. The NREL uses a cost scaling exponent of 0.7.

$$\text{New Cost} = \text{Original Cost} \left(\frac{\text{New Size}}{\text{Old Size}} \right)^{\text{exp}} \quad (16)$$

Plant Size and Collection Distance: The distance traveled to collect corn stover increases as the plant size increases because more stover is required for feed. This collection distance is estimated as the radius of a circle around the plant within which the stover is purchased. This area around the plant is calculated using the Equation 17.

$$\text{Area}_{\text{collection}} = \left(D_{\text{stover}} / \left(Y_{\text{stover}} * F_{\text{availableacres}} * F_{\text{landincrops}} \right) \right) \quad (17)$$

where: $\text{Area}_{\text{collection}}$ is the circle of collection around the plant

D_{stover} is the annual demand for stover by an ethanol plant

Y_{stover} is metric tons stover collected per acre per year

$F_{\text{availableacres}}$ is the fraction of total farmland from which stover can be collected

$F_{\text{landincrops}}$ is the fraction of surrounding farmland containing crops

The fraction of available acres takes into account the land use due to roads and buildings within the farm land. For example, if the farm area has 25% roads and other infrastructure, then the fraction of available land, $F_{\text{availableacres}}$, is 0.75. The $F_{\text{landincrops}}$ is a variable parameter depending on the ability of farms around the ethanol plant to contribute to the corn stover demand. The parameter is used to vary the dependence of plant size on collection distance, and the results are given in the Figure 39, with $F_{\text{landincrops}}$ having values 0.10, 0.50 and 1. The radius of collection is calculated from the $\text{Area}_{\text{collection}}$. The radius of collection is assumed as a rule of thumb in this design. The price of ethanol as a function of plant size and percentage of available acres is given in the Figure 40.

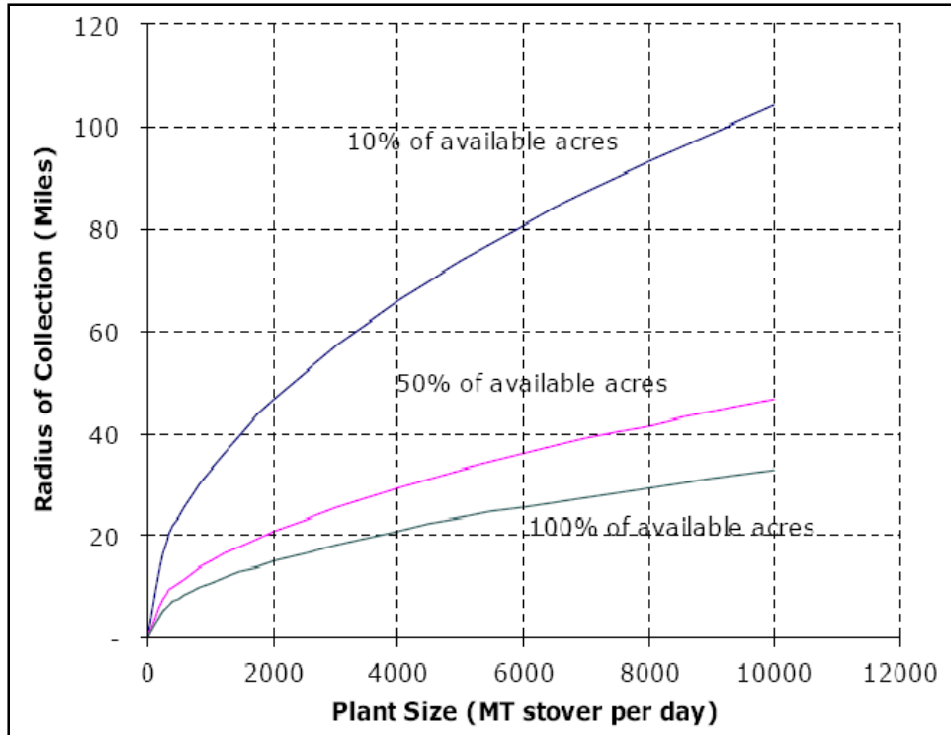


Figure 39 Effect of Plant Size on Collection Distance (Aden et al., 2002)

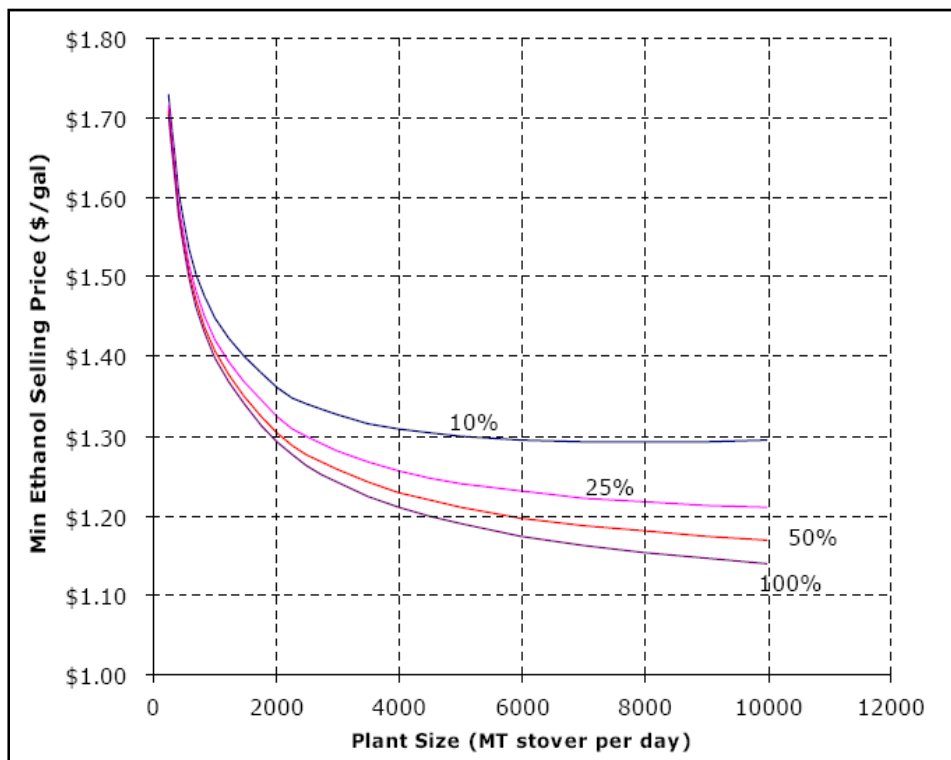


Figure 40 Ethanol Price as a Function of Plant Size and Percentage Available Acres (Aden et al., 2002)

Corn Stover Cost: The corn stover raw material cost depends on two direct costs; the cost of baling and staging stover at the edge of the field, and the cost of transportation from the field to the plant gate. Apart from these, a farmer's premium and cost for fertilizers also add up to the direct costs for corn stover as a raw material. A life cycle analysis of the corn stover represents that 47% of cost was in the staging and baling process, 23% was for transport of stover to plant, 11% was farmer premium for taking the risk of added work of collecting and selling the residue and the rest 12% for fertilizer supplement for the land. This method of analysis gave a value of \$62 per dry metric ton of corn stover. The report suggests that this cost will be reduced considerably over time, and an assumption of \$33 per dry metric ton of corn stover is taken for further analysis. This assumption is based on the ongoing research at the Oak Ridge National Laboratory. There are uncertainties in the calculation of premium to the farmer and nitrogen fertilizer costs (due to varying ammonia prices) which affect the cost of the stover.

The corn stover hauling cost (cost for farm to gate of plant) depended on distance from plant and the relationship is given in the Figure 41. The hauler cost is a function of radial distance from the plant. An increase in hauling cost shows the optimum plant size range to decrease. Figure 42 gives the ethanol price as a function of plant size and hauling cost. For 50% increase in hauling costs per ton-mile, plant size range decreases from 2000-8000 m.t./day to 2000-5000 m.t./day. For a 100% increase, the optimal plant size is at around 3000 m.t./day and the price of ethanol increases drastically above or below the price shown in Figure 40.

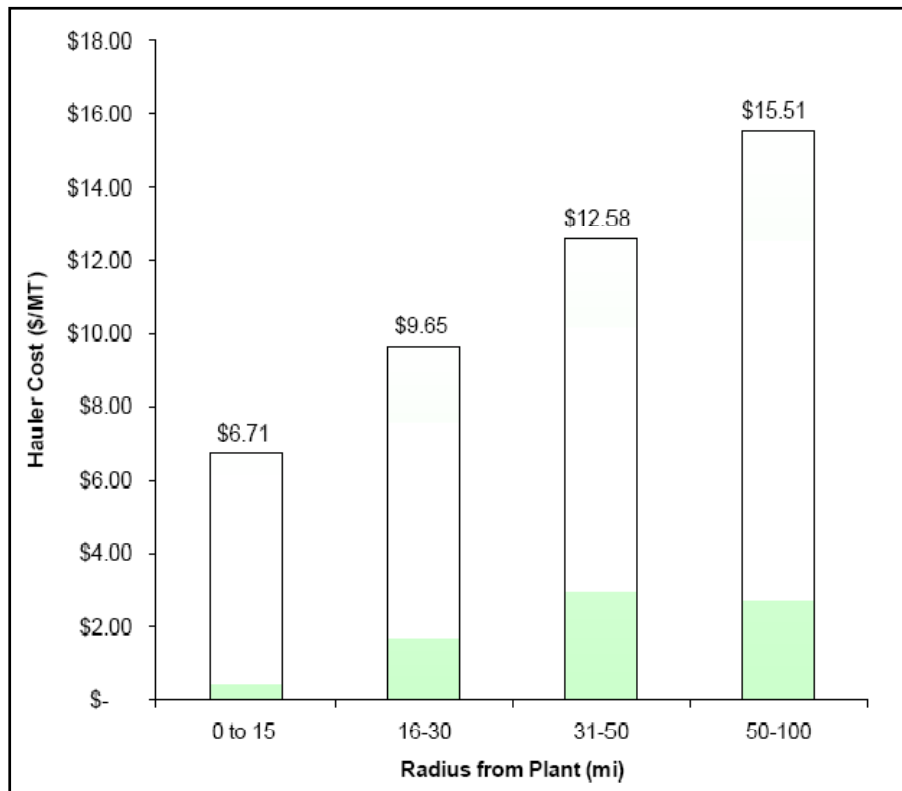


Figure 41 Hauling charges as a function of distance (Aden et al., 2002)

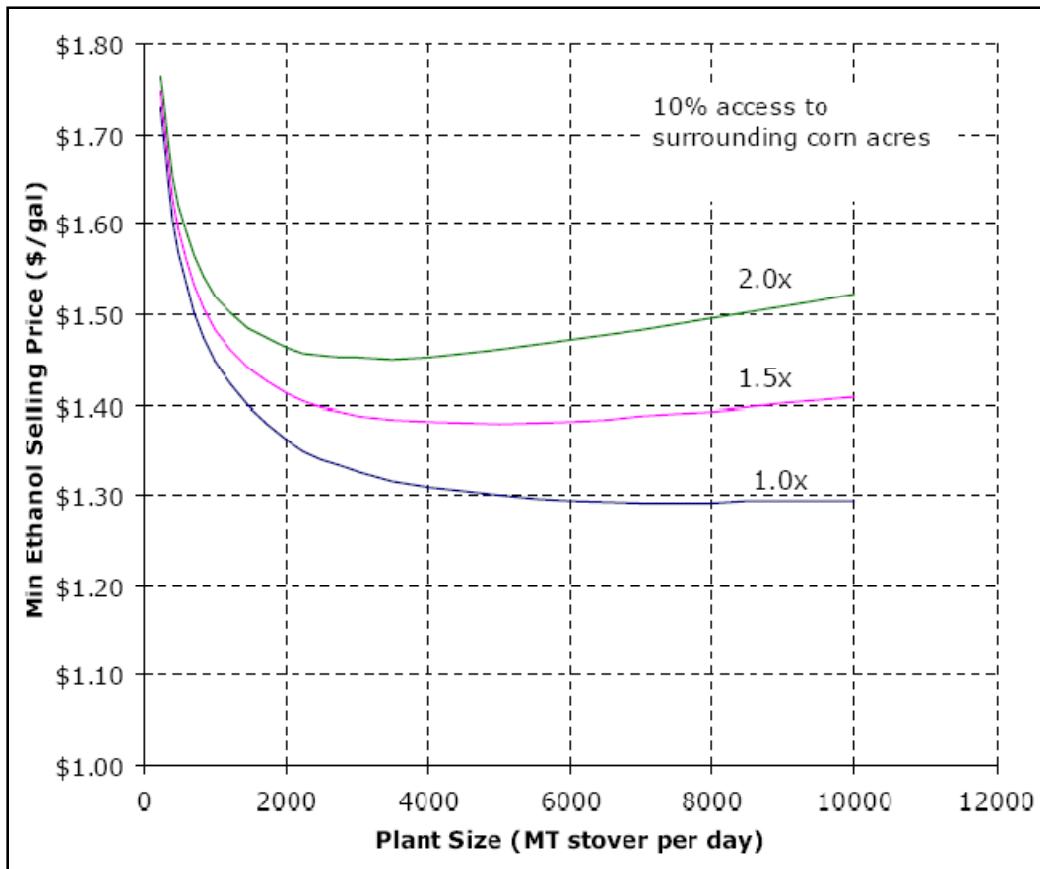


Figure 42 Ethanol Price as a Function of Plant Size and Hauling Cost for 10% Access (Aden et al., 2002)

Total Cost of Ethanol as a Function of Plant Size: The total cost of ethanol as a function of plant size is determined with the total feedstock and non-feedstock costs. This is given in Figure 43. The analysis was done with two plant sizes of 2000 and 10000 m.t./day of stover. From Figure 43, a net savings occurs for plant sizes between 6000 and 8000 m.t./day of stover. Below 2000 m.t./day, the selling price per gallon of ethanol increases rapidly. A minimum optimal plant size between 2000 and 4000 m.t./day of corn stover was obtained for collection from 10% corn acres around a conversion plant.

Ethanol from Glycerol: Ito et al., 2005 describes a process where ethanol is produced from glycerol containing waste discharged after transesterification process. *Enterobacter aerogenes* HU-101 microorganism is used to ferment the glycerol-rich waste and yields of 63mmol/l/h of H₂ and 0.85mole ethanol per mole glycerol were reported using porous ceramics as support to fix cells in the reactor.

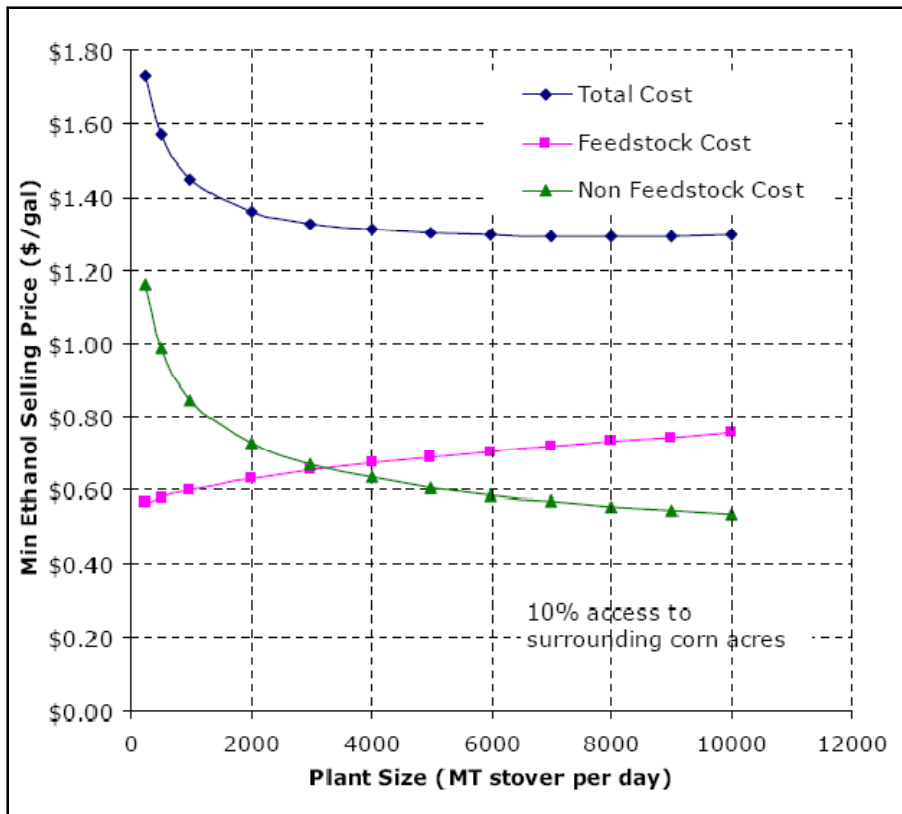


Figure 43 Ethanol Cost as a Function of Plant Size (Aden et al., 2002)

Ethanol from Synthesis Gas Fermentation: Synthesis gas can be used as feed to a fermenter that uses an anaerobic bacterial to produce ethanol. Although it uses some of the oldest biological mechanisms in existence, technical barriers to be overcome include organism development, gas-liquid mass transfer and product yield (Snyder, 2007).

Spath et al., 2003 gives a detailed description of the process for conversion of synthesis gas to ethanol. The first step in the process is to produce biomass synthesis gas. The syngas is then converted to ethanol using fermentation. The feedstock for this process is wood chips derived from forestry. The overall schematic diagram is given in Figure 44. The feed is first received and placed in temporary storage on-site. The biomass feed is dried and then fed to a fast fluidized bed where it is converted into a raw syngas mixture rich in CO and hydrogen. An indirect BCL/FERCO process gasifier is used for the production of syngas from biomass. Typical operating conditions are 700-850 °C at pressures slightly greater than atmospheric. The design produces a medium-BTU syngas, without the need for an oxygen plant.

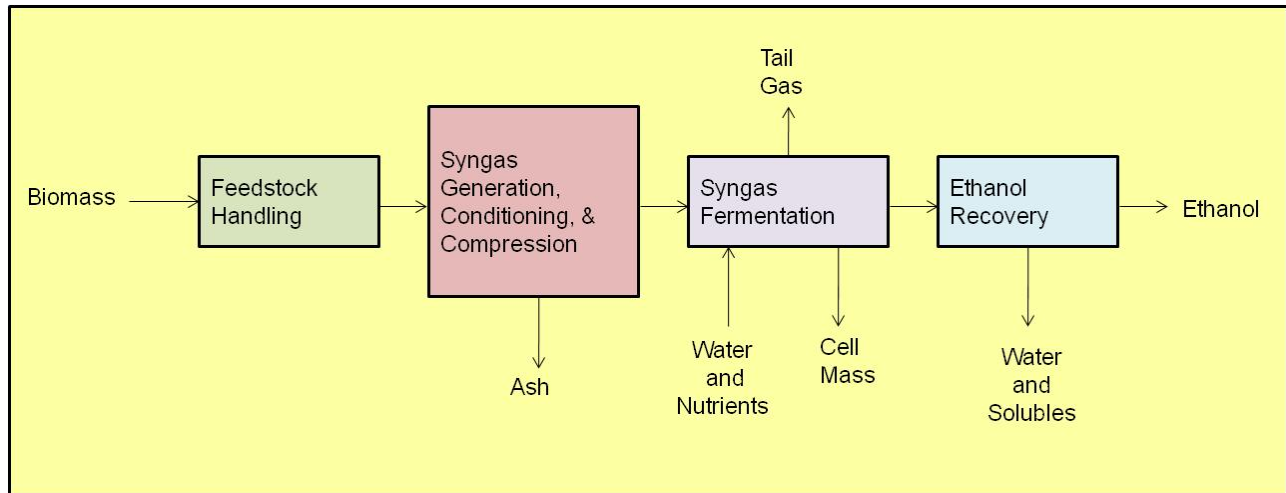


Figure 44 Synthesis Gas to Ethanol Process (Spath et al., 2003)

Circulating sand provides heat for the gasification in this bed. The resulting syngas is sent downstream for further conditioning and compression. The disengaged sand and char obtained by a cyclone separator is fed to a second fluidized bed where it is mixed with air and the char is combusted. The heat released in the combustor is used to heat the circulating sand. Heat is also recovered in the combustor off-gas and used either for drying or for steam generation.

The resulting syngas contains significant amounts of methane, ethylene and other light hydrocarbons and tars. These species can be removed in the gas conditioning steps, converted to additional syngas in the gas-conditioning step, or allowed to pass through the fermentation for eventual incineration with the fermentation tail gas as a fuel trim to the combustion section of the gasifier.

The conditioned syngas is then fed to fermentation reactors where it is converted to ethanol using bacteria. The resulting fermentation broth is quite dilute, typically containing 2% or less of ethanol. The ethanol can be recovered from the broth using recovery schemes used in the existing corn ethanol industry (i.e. an ethanol-water mixture close to the azeotropic composition is distilled overhead and an adsorption unit is used to further dry the ethanol product to meet fuel grade specification on water content). The cell mass produced can be recycled as a portion of the feed to the gasifier. One advantage of the syngas fermentation route is that the chemical energy stored in all parts of the biomass, including the lignin fraction, contributes to the yield of ethanol. Equation 18 gives the method to calculate the capacity of ethanol produced by this process.

$$P = \frac{F \times HHV_F \times \eta_{Gas+Cond} \times X_{CO+H_2 / EtOH}}{1.5 \times 10^5} \quad (18)$$

where: P = Production of ethanol, million gal/yr

F = Feed rate, tons/day (dry basis)

HHV_F = Higher heating value of the feed in Btu/lb (dry)

$\eta_{Gas+Cond}$ = Cold gas efficiency of gasifier + conditioning steps (a fraction less than 1)

$X_{CO+H_2/EtOH}$ = Average conversion of CO and H₂ to ethanol, as a fraction of theoretical

Spath et al., 2003 gave the overall reactions for the process as given in Equation 19, 20, 21 and 22. The micro-organisms used for ethanol production from syngas mixtures are anaerobes that use a heterofermentative version of the acetyl-CoA pathway for acetogenesis. Acetyl-CoA is produced from CO or H₂/CO₂ mixtures in this pathway. The acetyl-CoA intermediate is then converted into either acetic acid or ethanol as a primary metabolic product.



Spath et al., 2003 also gave the cost analysis for the gasification process and fermentation. A facility for gasification that processes 2,000 tons (dry) per day of wood would produce 48.5 million gal/yr of ethanol based on an ethanol yield of 71 gallons per ton. Fixed capital was estimated at \$153.6 million, or \$3.17 per annual gallon of capacity. Costs were \$0.697 per gallon with feedstock cost at \$25 per ton. The price required for a zero net present value for the project with 100% financing and 10% real after-tax discounting, known as rational cost, was \$1.33 per gallon.

Acetic Acid: Acetic acid was first made by the fermentation of ethyl alcohol and a very dilute solution of it is used as vinegar (Wells, 1999). Small quantities of acetic acid are recovered from pyroligneous acid liquor obtained from the destructive distillation of hard wood. The modern acetic acid industry began with the commercial availability of acetylene which was converted to acetaldehyde and then oxidized to acetic acid. The three commercial processes for the manufacture of acetic acid are oxidation of acetaldehyde, liquid phase oxidation of n-butane or naphtha and carbonylation of methyl alcohol. The carbonylation of methyl alcohol is the dominant technology because of low material and energy costs and the absence of significant by-products. Synthesis gas is the raw material for the carbonylation process at low temperature and pressure using a proprietary catalyst, rhodium iodide, developed by BASF and Monsanto. The synthesis gas can be produced alternately from biobased feedstock using gasification and pyrolysis as described in the previous section. Capacities of acetic acid plants range from 30,000 – 840,000 tons per year.

According to Wells, 1999, 44% of acetic acid is converted to vinyl acetate which is used to form polyvinyl acetate and polyvinyl alcohols used for paints, adhesives and plastics. 12% of acetic acid is converted to acetic anhydride which is used to manufacture cellulose acetate, paper sizing agents, a bleach activator and aspirin. 13% of acetic acid is used to produce acetates and esters used in solvents for coatings, inks, resins, gums, flavorings and perfumes. 12% of acetic acid is used in the production of terephthalic acid (TPA) used for polyethylene terephthalate (PET) bottles and fibers.

Cellulose acetate is a cellulose derivative prepared by acetylating cellulose with acetic anhydride (Wells, 1999). Fully acetylated cellulose is partially hydrolyzed to give an acetone soluble product, which is usually between a di- and a tri-ester (Austin, 1984). The esters are mixed with plasticizers, dyes and pigments and processed in different ways depending on the form of plastic desired.

The important properties of cellulose acetate include mechanical strength, impact resistance, transparency, colorability, fabricating versatility, moldability, and high dielectric strength (Austin, 1984). Cellulose acetate is used to manufacture synthetic fibers like rayon, and is based on cotton or tree pulp cellulose.

Research has been reported using waste cellulose from corn fiber, rice hulls and wheat straw to produce cellulose acetate (Ondrey, 2007b). The raw materials are milled, slurried in dilute sulfuric acid and pretreated in an autoclave at 121 °C. This is followed by the acetylation to cellulose triacetate under ambient conditions at 80 °C., using acetic acid, acetic anhydride, methylene chloride and trace amounts of sulfuric acid. The cellulose acetate is soluble in methylene chloride and separated easily from the reaction medium. Conversions of cellulose to cellulose acetate have been 35-40% in a laboratory study. The incentive to pursue this line of work was the price of cellulose acetate, approximately \$2.00 per pound, a more valuable product than ethanol.

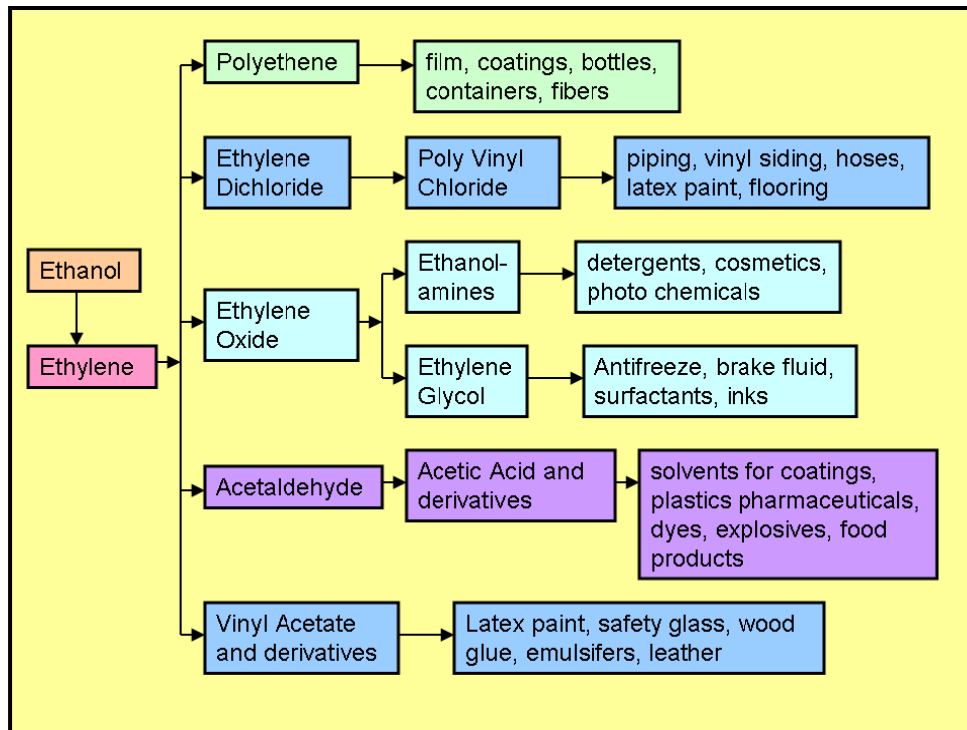


Figure 45. Ethanol as a Raw Material for the Ethylene Product Chain (Pellegrino, 2000)

Ethylene: Ethylene ranks fourth among chemicals produced in large volumes in the United States with about 48 billion pounds produced in 1997 (Pellegrino, 2000). It is a principal building block for the petrochemicals industry, with almost all of the ethylene produced being used as a feedstock in the manufacture of a wide variety of chemicals and polymers as was shown in Figure 45. Polyethylene (PE) is used in the manufacture of plastic films, packaging

materials, moldings (e.g., toys, chairs, automotive parts, and beverage containers), wire and cable insulation, pipes, and coatings. Production of polyethylene in 1997 was about 27 billion pounds. Ethylene dichloride is used to manufacture poly vinyl chloride (PVC) which is used in drainage and sewer pipes, electrical conduits, industrial pipes, wire and cable coatings, wall panels, siding, doors, flooring, gutters, downspouts, and insulation. U.S. chemicals production of ethylene dichloride was over 20 billion pounds in 1997. U.S. production of PVC was about 14 billion pounds in 1997. Ethylene oxide is used for the production of ethylene glycol which is commonly used in antifreeze. Ethylene glycol also serves as a raw material in the production of polyester, used for manufacturing textiles. Ethylene oxide and ethylene glycol are both listed among the top fifty chemicals produced in the United States, with ethylene oxide ranking twenty-seventh (7.1 billion pounds in 1997) and ethylene glycol ranking twenty-ninth (5.6 billion pounds in 1997).

World demand for ethylene was about 180 billion pounds in 1998, and was predicted to reach 250 billion pounds by 2005 (Pellegrino, 2000). The United States is currently the largest ethylene-producing country in the world, with the Western European countries close behind in second place. The polyethylene industry was a 100 billion pound market with over 150 producers worldwide in 1998. The global market for poly vinyl chloride was estimated at about 7.5 billion pounds capacity.

The petroleum refining industry is the major supplier of raw materials for ethylene production, and a large percentage of ethylene capacity is located at petroleum refineries that are in close proximity to petrochemical plants (Pellegrino, 2000). Currently about 20 percent of ethylene is produced from naphtha (a light petroleum fraction) and 10 percent from gas oil from refinery processing units. In Western Europe and some Asian countries (South Korea, Taiwan, Japan), naphtha and gas oil account for 80 to 100 percent of the feed to ethylene crackers. Overall, more than 50 percent of ethylene production capacity is currently located at refineries. However, the current resources of petroleum are being depleted for use as fuels and the rising price of petroleum feedstock open up new areas for research for the production of ethylene.

Ethanol can be used for the production of ethylene by dehydrogenation (Wells, 1999). Ethanol is vaporized by preheating with high pressure steam before passing over a fixed bed of activated alumina and phosphoric acid or alumina and zinc oxide contained in a reactor. The reactor can be isothermal or adiabatic, with temperature maintained at 296-315 °C. The reaction is endothermic and the heat is supplied by condensing vapor latent heat. The temperature control in the reactor is important to prevent the formation of acetaldehyde or ethers as byproducts. The gas is purified, dried and compressed using conventional steps. A fluidized bed modification of this process has been developed with efficient temperature controls and conversions up to 99%.

Takahara et al., 2005 has discussed the use of different catalysts for the dehydrogenation of ethanol into ethylene. The dehydration of ethanol into ethylene was investigated over various solid acid catalysts such as zeolites and silica–alumina at temperatures ranging from 453 to 573 K under atmospheric pressure. Ethylene was produced via diethyl ether during the dehydration process. H-mordenites were the most active media for the dehydration.

Three-Carbon Compounds

Glycerol: Glycerin (glycerol) is a triol occurring in natural fats and oils. About 90% of glycerol is produced from natural sources by the transesterification process. The other 10% is commercially manufactured synthetically from propylene (Wells, 1999).

Glycerol is a major byproduct in the transesterification process used to convert vegetable oils to FAME and FAEE. Approximately 10% by weight of glycerol is produced for the transesterification of soybean oil with an alcohol. Transesterification process is used to manufacture fatty acid methyl and ethyl esters which can be blended in refinery diesel. As the production of FAEE and FAME increases, the quantity of glycerol manufactured also increases the need to explore cost effective routes to convert glycerin to value-added products.

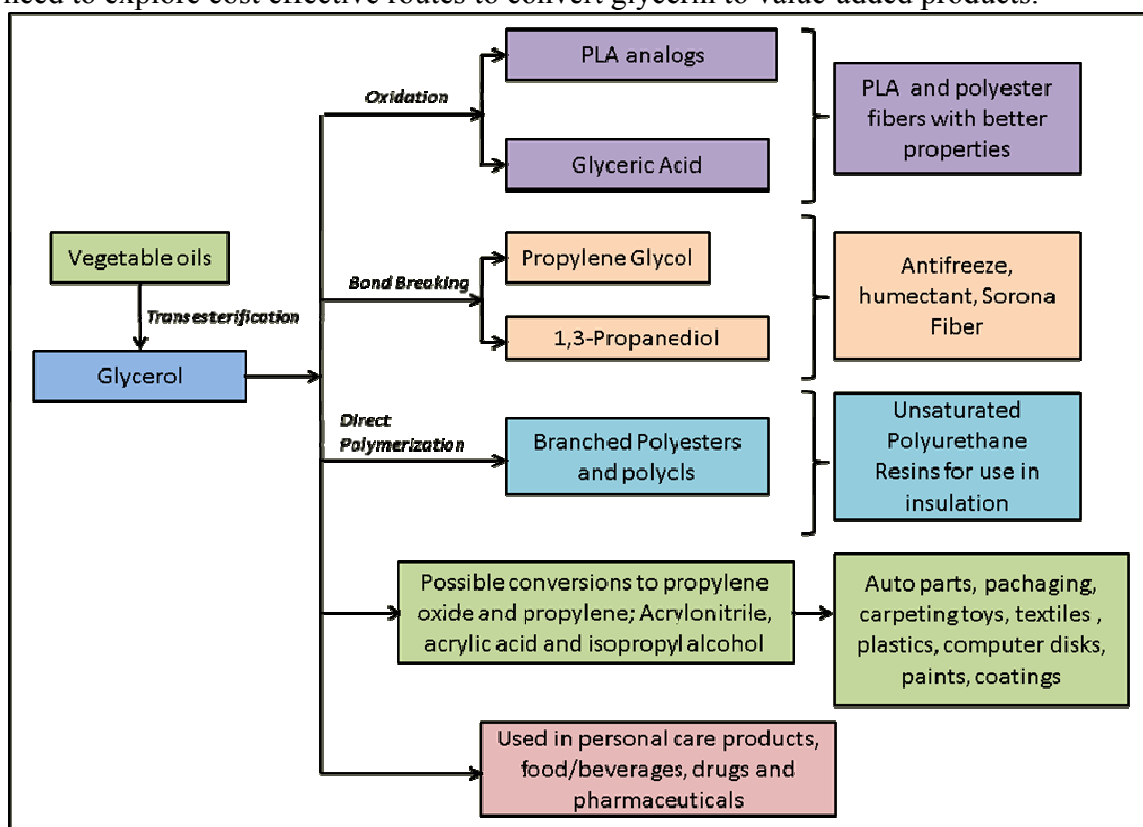


Figure 46. Production and Derivatives of Glycerol (Werpy et al., 2004; Pellegrino, 2000)

Glycerol currently has a global production of 500,000–750,000 tons/year (Werpy et al., 2004). The United States is one of the world’s largest suppliers and consumers of refined glycerol. Referring to Figure 46, glycerin can potentially be used in a number of paths for chemicals that are currently produced from petroleum based feedstock. Glycerol and various simple derivatives of glycerol (such as glycerol triacetate, glycerol stearate, and glycerol oleate) are currently produced by the chemical industry at companies such as Uniqema, Procter and Gamble, and Stephan. Glycerol prices could drop to \$0.05/lb, enabling its availability as a cheap feedstock for conversion to chemicals. Small increases in fatty acid consumption for fuels and products can increase world glycerol production significantly. For example, if the United States

displaced 2% of the on-road diesel with biodiesel by 2012, almost 800 million pounds of new glycerol supplies would be produced.

Dasari, et al., 2005 reported a low pressure and temperature (200 psi and 200°C) catalytic process for the hydrogenolysis of glycerol to propylene glycol that is being commercialized and received the 2006 EPA Green Chemistry Award. Copper-chromite catalyst was identified as the most effective catalyst for the hydrogenolysis of glycerol to propylene glycol amongst nickel, palladium, platinum, copper, and copper-chromite catalysts. The low pressure and temperature are the advantages for the process when compared to traditional process. The mechanism proposed forms an acetol intermediate in the production of propylene glycol. In a two-step reaction process, the first step of forming acetol can be performed at atmospheric pressure while the second requires a hydrogen partial pressure. Propylene glycol yields >73% were achieved at moderate reaction conditions.

Karinen et al., 2006 studied the etherification of glycerol with isobutene in liquid phase with acidic ion exchange resin catalyst. Five product ethers and a side reaction yielding C₈-C₁₆ hydrocarbons from isobutene were reported. The optimal selectivity towards the ethers was discovered near temperature of 80°C and isobutene/glycerol ratio of 3. The reactants for this process were isobutene (99% purity), glycerol (99% purity) and pressurized with nitrogen (99.5% purity). The five ether isomers formed in the reaction included two mono-substituted monoethers (3-tert-butoxy-1,2-propanediol and 2-tert-butoxy-1,3-propanediol), two di-substituted diethers (2,3-di-tert-butoxy-1-propanol and 1,3-di-tert-butoxy-2-propanol) and one tri-substituted triether (1,2,3-tri-tert-butoxy propane). *Tert*-butyl alcohol was added in some of the reactions to prevent oligomerization of isobutene and improve selectivity towards ethers.

Lactic acid: Lactic acid is a commonly occurring organic acid, which is valuable due to its wide use in food and food-related industries, and its potential for the production of biodegradable and biocompatible polylactate polymers. Lactic acid can be produced from renewable materials using various fungal species of the *Rhizopus* genus, which have advantages compared to the bacteria, including their amylolytic characteristics, low nutrient requirements and valuable fermentation by-product—fungal biomass (Zhang et al., 2007).

Lactic acid can be produced using bacteria and fungi. Lactic acid producing bacteria (LAB) have high growth rate and product yield. However, LAB has complex nutrient requirements because of their limited ability to synthesize B-vitamins and amino acids. They need to be supplemented with sufficient nutrients such as yeast extracts to the media. This downstream process is expensive and increases the overall cost of production of lactic acid using bacteria.

BASF uses 45% corn based polylactic acid for its product Ecovio® (BASF, 2007).

Propylene Glycol: Propylene glycol is industrially produced from the reaction of propylene oxide and water (Wells, 1999). Capacities of propylene glycol plants range from 15,000 to 250,000 tons per year. It is mainly used (around 40%) for the manufacture of polyester resins which are used in surface coatings and glass fiber reinforced resins. A rapidly growing market for propylene glycol is in the manufacture of non-ionic detergents (around 7%) used in

petroleum, sugar and paper refining and also in the preparation of toiletries, antibiotics, etc., and 5% of propylene glycol manufactured is used in antifreeze.

Propylene glycol can be produced from glycerol, a byproduct of transesterification process, by a low pressure and temperature (200 psi and 200°C) catalytic process for the hydrogenolysis of glycerol to propylene glycol (Dasari, et al., 2005) that is being commercialized and received the 2006 EPA Green Chemistry Award.

Ashland, Inc and Cargill have a joint venture underway to produce propylene glycol in a 65,000 m.t./yr plant in Europe (Ondrey, 2007a,c). Davy Process Technology Ltd. (DPT) has developed the glycerin to propylene glycol process for this plant. The plant is expected to startup in 2009. The process is outlined in Figure 47. This is a two step process where glycerin in the gas phase is first dehydrated into water and acetol over a heterogeneous catalyst bed, and then, propylene glycol is formed in situ in the reactor by the hydrogenation of acetol. The per pass glycerin conversion is 99% and byproducts include ethylene glycol, ethanol and propanols.

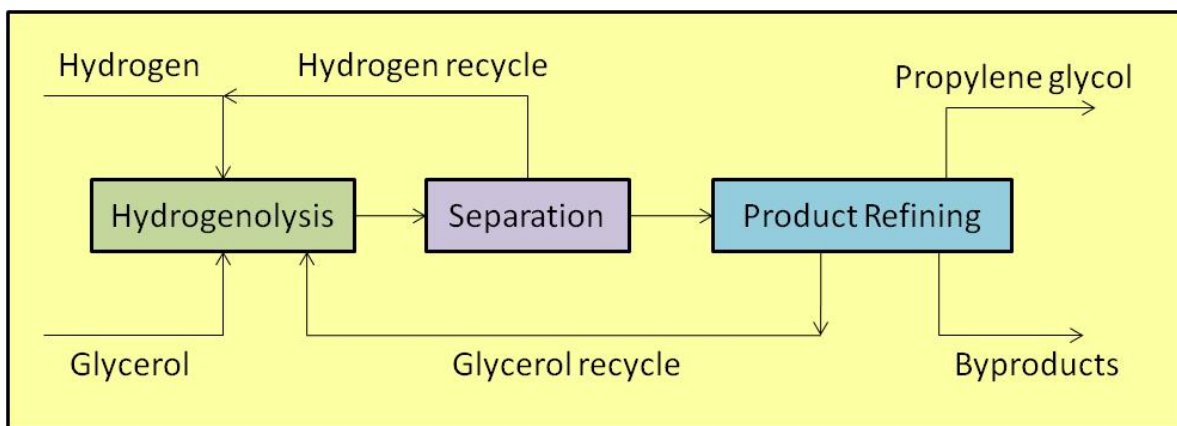


Figure 47 DPT Process for Manufacture of Propylene Glycol from Glycerol by Hydrogenolysis (Ondrey, 2007a)

Huntsman Corporation plans to commercialize a process for propylene glycol from glycerin at their process development facility in Conroe, Texas (Tullo, 2007b). Dow and Solvay are planning to manufacture epoxy resin raw material epichlorohydrin from a glycerin-based route to propylene glycol.

1,3-Propanediol: 1,3-Propanediol is a derivative that can be used as a diol component in the plastic polytrimethyleneterephthalate (PTT), a new polymer comparable to nylon (Wilke et al., 2006). 1,3-propanediol can be prepared from glycerol by bacterial treatment and from glucose by mixed culture of genetically engineered microorganisms. Also, Shell produces propanediol from ethylene oxide and Degussa produces it from acrolein. It is used by Shell under the name Corterra to make carpets and DuPont under the name Sorona to make special textile fibers.

DuPont Tate and Lyle Bio Products, LLC opened a \$100 million facility in Loudon, Tennessee to make 1,3-propanediol from corn (CEP, 2007). The company uses a proprietary fermentation process to convert the corn Bio-PDO, the commercial name of 1,3-propanediol used by the company. This process uses 40% less energy and reduces greenhouse gas emissions by 20% compared with petroleum-based propanediol.

Mu et al., 2006 gives a process for conversion of crude glycerol to propanediol. They conclude that a microbial production of 1,3-PD by *K. pneumoniae* was feasible by fermentation using crude glycerol as the sole carbon source. Crude glycerol from the transesterification process could be used directly in fed-batch cultures of *K. pneumoniae* with results similar to those obtained with pure glycerol. The final 1,3-PD concentration (53 g/l) of glycerol from lipase-catalyzed methanolysis of soybean oil was comparable to that of glycerol from alkali-catalyzed process (51.3 g/l). Considering the high 1,3-PD concentration and volumetric productivity from crude glycerol, a low fermentation cost would be expected, which is an important factor for the bioconversion of such industrial byproducts into valuable compounds.

A microbial conversion process for propanediol from glycerol using *Klebsiella pneumoniae* ATCC 25955 was given by Cameron et al., 1994. A \$0.20/lb of crude glycerol raw material cost, a product selling price of \$1.10/lb of pure diol and with a capital investment of \$15 MM, a return on investment of 29% was obtained. The price of raw material has gone down considerably since then, and a higher return on investment can be expected for future propanediol manufacturing processes.

Four-Carbon Compounds

Butanol: Butanol or butyl alcohol can be produced by the fermentation of carbohydrates with bacteria yielding a mixture of acetone and butyl alcohol (Wells, 1999). Synthetically, butyl alcohol can be produced by the hydroformylation of propylene, known as the oxo process, followed by the hydrogenation of the aldehydes formed yielding a mixture of n- and iso- butyl alcohol. The use of rhodium catalysts maximizes the yield of n-butyl alcohol. The principal use of n-butyl alcohol is as solvent. Butyl alcohol/butyl acetate mixtures are good solvents for nitrocellulose lacquers and coatings. Butyl glycol ethers formed by the reaction of butyl alcohol and ethylene oxide are used in vinyl and acrylic paints and lacquers, and to solubilize organic surfactants in surface cleaners. Butyl acrylate and methacrylate are important commercial derivatives that can be used in emulsion polymers for latex paints, in textile manufacturing and in impact modifiers for rigid polyvinyl chloride. Butyl esters of acids like phthalic, adipic and stearic acid can be used as plasticizers and surface coating additives.

Butanol can be produced from biomass by fermentation. DuPont and BP are working with British Sugar to produce 30,000 m.t./yr of biobutanol using corn, sugarcane or beet as feedstock. U.K. biotechnology firm Green Biologics has demonstrated the conversion of cellulosic biomass to butanol, known as Butafuel. Butanol can also be used as a fuel additive instead of ethanol (D'Aquino, 2007). When compared to ethanol, butanol is less volatile, not sensitive to water, less hazardous to handle, less flammable, has a higher octane number and can be mixed with gasoline in any proportion. The production cost of butanol from biobased feedstock is reported to be \$3.75/gallon.

Succinic Acid: Succinic acid, a DOE top thirty candidate, is an intermediate for the production of a wide variety of chemicals as shown in Figure 48. Succinic acid is produced biochemically from glucose using an engineered form of the organism *A. succiniciproducens* or an engineered *Eschericia coli* strain developed by DOE laboratories (Werpy et al., 2004).

Zelder, 2006 discussed BASF's efforts to develop bacteria that convert biomass to succinate and succinic acid. The bacteria converts the glucose and carbon dioxide with an almost 100 percent yield into the C4 compound succinate. BASF is also developing a chemistry that will convert the fermentation product into succinic acid derivatives, butanediol and tetrahydrofuran. Succinic acid can also be used as a monomeric component for polyesters.

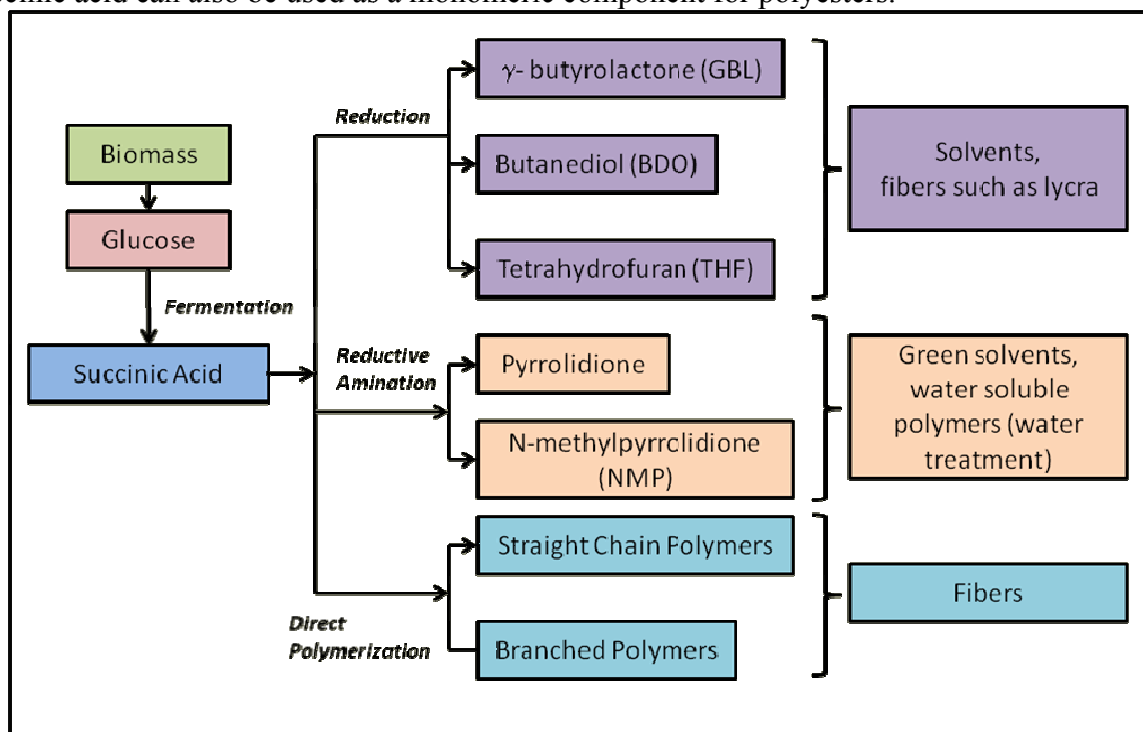


Figure 48 Succinic Acid Production and Derivatives (Werpy et al., 2004)

Snyder, 2007 reports the successful operation of a 150,000 liter fermentation process that uses a licensed strain of *E. coli* at the Argonne National Laboratory. Opportunities for succinic acid derivatives include maleic anhydride, fumaric acid, dibase esters and others in addition to the ones shown in Figure 48.

The overall cost of fermentation is one of the major barriers to this process. Low cost techniques are being developed to facilitate the economical production of succinic acid (Werpy et al., 2004).

Bioamber, a joint venture of Diversified Natural Products (DNP) and Agro Industries Recherche et Development will construct a plant that will produce 5,000 metric tons/year of succinic acid from biomass in Pomacle, France (Ondrey, 2007d). The plant is scheduled for startup in mid-2008. Succinic acid from BioAmber's industrial demonstration plant is made from sucrose or glucose fermentation using patented technology from the U.S. Department of Energy

in collaboration with Michigan State University. Biomaber will use patented technology developed by Michael G.V. et al., 1996, for the production of succinic acid using biomass and carbon dioxide.

Aspartic acid: Aspartic acid is a α -amino acid manufactured either chemically by the amination of fumaric acid with ammonia or the biotransformation of oxaloacetate in the Krebs cycle with fermentative or enzymatic conversion (Werpy et al., 2004). It is one of the chemicals identified in DOE top 12 value added chemicals from biomass list. Aspartic acid can be used as sweeteners and salts for chelating agents. The derivatives of aspartic acid include amine butanediol, amine tetrahydrofuran, aspartic anhydride and polyaspartic with new potential uses as biodegradable plastics.

Five-Carbon Compounds

Levulinic Acid: Levulinic acid is one of the top 30 building block chemicals from biomass identified by DOE (Werpy and Peterson, 2004) that can be produced from hemicellulose in aquatic and other biomass. Levulinic acid (LA) is formed by treatment of 6-carbon sugar carbohydrates from starch or lignocellulosics with acid. Five carbon sugars derived from hemicelluloses like xylose and arabinose can also be converted to levulinic acid by addition of a reduction step subsequent to acid treatment. The following steps can be used for the production of levulinic acid (Klass 1998). Xylose from hemicelluloses is dehydrated by acid treatment to yield 64 wt % of furan-substituted aldehyde (furfural). Furfural undergoes catalytic decarbonylation to form furan. Furfuryl alcohol is formed by catalytic hydrogenation of the aldehyde group in furfural. Tetrahydrofurfuryl alcohol is formed after further catalytic hydrogenation of furfural. Levulinic acid (γ -ketovaleric acid) is formed from tetrahydrofurfuryl alcohol on treatment with dilute acid. Werpy et al., 2004 reports an overall yield of 70% for production of levulinic acid.

Levulinic acid is a key intermediate for commodity chemicals as shown in Figure 49. It can be reduced to methyl tetrahydrofuran and butyrolactone which can be used as fuel additives or solvents (Werpy and Peterson, 2004). The levulinic acid can be oxidized to acetyl acrylates which can be used in copolymerization. It can also be directly polymerized to diphenolic acids.

Levulinic acid was first synthesized from fructose with hydrochloric acid by the Dutch scientist G.J. Mulder in 1840 (Kamm et al., 2006). It is also known as 4-oxopentanoic acid or γ -ketovaleric acid. In 1940, the first commercial scale production of levulinic acid in an autoclave was started in United States by A.E. Stanley, Decatur, Illinois. Levulinic acid has been used in food, fragrance and specialty chemicals. The derivatives have a wide range of applications like polycarbonate resins, graft copolymers and biodegradable herbicide.

A number of large volume chemical markets can be addressed from the derivatives of levulinic acid (Werpy et al., 2004). In Figure 49 the production of levulinic acid is shown from hemicellulose. Also shown are the derivatives of levulinic acid. In addition to the chemicals in the figure, the following derivative chemicals of levulinic acid also have a considerable market. Methyltetrahydrofuran and various levulinate esters can be used as gasoline and biodiesel additives, respectively. δ -aminolevulinic acid is a herbicide, and targets a market of 200 – 300 million lb/yr at a projected cost of \$2.00-3.00/lb. An intermediate in the production of δ -aminolevulinic acid is β -acetylacrylic acid. This material could be used in the production of new

acrylate polymers, addressing a market of 2.3 billion lb/yr with values of about \$1.30/lb. Diphenolic acid is of particular interest because it can serve as a replacement for bisphenol A in the production of polycarbonates. The polycarbonate resin market is almost 4 billion lb/yr, with product values of about \$2.40/lb. New technology also suggests that levulinic acid could be used for production of acrylic acid via oxidative processes. LA is also a potential starting material for production of succinic acid. Production of levulinic acid-derived lactones offers the opportunity to enter a large solvent market, as these materials could be converted into analogs of N-methylpyrrolidone. Complete reduction of levulinic acid leads to 1,4-pentanediol, which could be used for production of new polyesters.

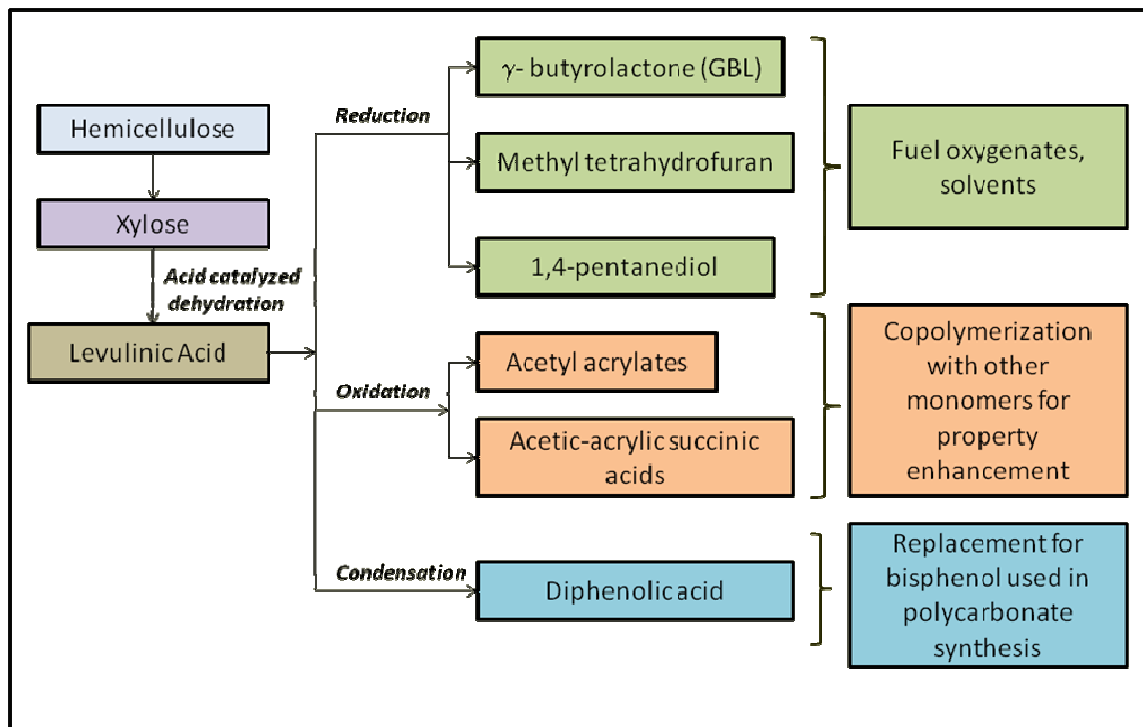


Figure 49 Production and Derivatives of Levulinic Acid (Werpy et al., 2004)

A levulinic acid production facility has been built in Caserta, Italy by Le Calorie, a subsidiary of Italian construction company Immobili (Ritter, 2006). The plant is expected to produce 3000 tons/yr of levulinic acid from local tobacco bagasse and paper mill sludge through a process developed by Biofine Renewables.

Hayes et al., 2006 gives the details of the Biofine process for the production of levulinic acid. This process received the Presidential Green Chemistry Award in 1999. The Biofine process involves a two step reaction in a two reactor design scheme. The feedstock is 0.5-1.0 cm biomass particles of cellulose and hemicellulose conveyed to a mixing tank by a high-pressure air-injection system. The feed is mixed with 2.5-3% recycled sulfuric acid in the mixing tank. The feed is then transferred to the reactors. The first reactor is a plug flow reactor, where first-order acid hydrolysis of the carbohydrate polysaccharides occurs to form soluble intermediates like hydroxymethylfurfural (HMF). The residence time in the reactor is 12 seconds at a temperature of 210-220°C and pressure of 25 bar. The diameter of the reactor is small to enable a

short residence time. The second reactor is a back mix reactor operated at 190-200°C and 14 bar and a residence time of 20 minutes. levulinic acid is formed in this reactor favored by the completely mixed conditions of the reactor. Furfural and other volatile products are removed and the tarry mixture containing levulinic acid is passed to a gravity separator. The insoluble mixture from this unit goes to a dehydration unit where the water and volatiles are boiled off. The crude levulinic acid obtained is 75% purity and can be purified to 98%. The residue formed is a bone dry powdery substance or char with calorific value comparable to bituminous coal and can be used in syngas production. Lignin is another by-product which can be converted to char and burned or gasified. The Biofine process uses polymerization inhibitors which convert around 50% of both 5 and 6 carbon sugars to levulinic acid.

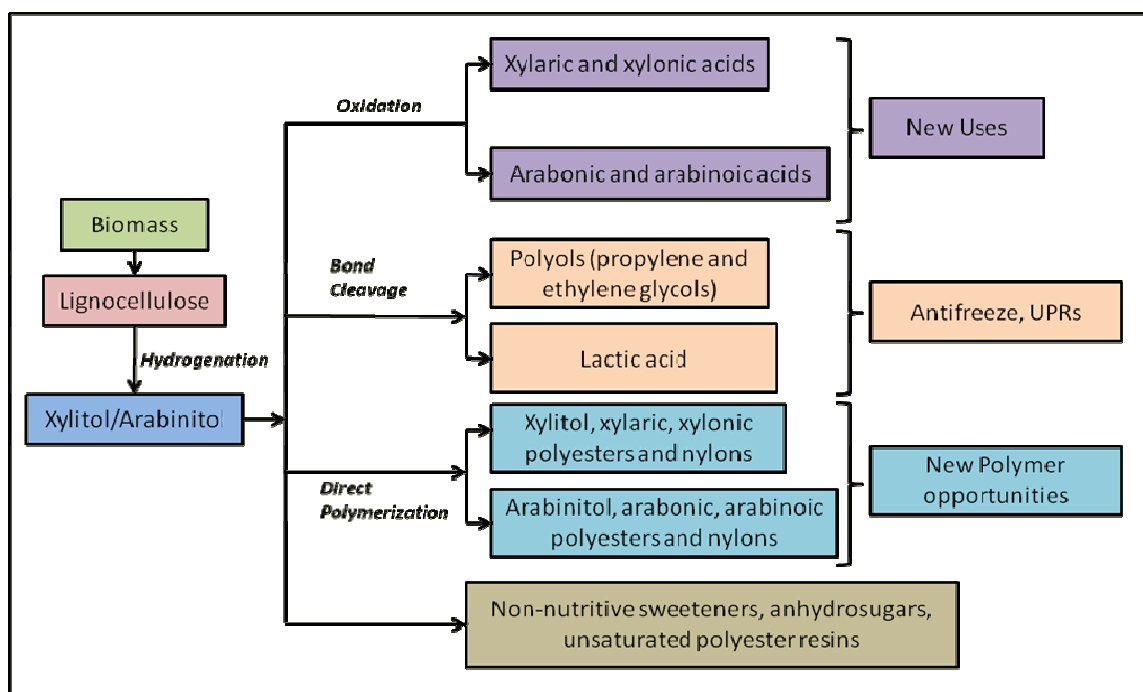


Figure 50 Production and Derivatives of Xylitol and Arabinitol (Werpy et al., 2004)

Xylitol/Arabinitol: Xylitol or arabinitol (pentanpentol - $C_5H_7(OH)_5$), a DOE top thirty candidate, can be produced from pretreatment of aquatic and other biomass sources and hydrogenation of sugars (Werpy and Peterson, 2004). These processes have almost no technical barriers. Xylitol can be oxidized to its acid derivatives. Direct polymerization or bond cleavage pathways can be used to obtain derivatives from xylitol. These derivatives currently have limited market demand except for antifreeze and glycols, but new uses are being evaluated. These processes can be integrated into the chemical production complex to provide intermediates for the C_4 chemical product chain. Derivatives of xylitol and arabinitol are shown in Figure 50.

Xylitol and arabinitol are hydrogenation products from the corresponding sugars xylose and arabinose (Werpy et al., 2004). Currently, there is limited commercial production of xylitol and no commercial production of arabinitol. The technology required to convert the five carbon sugars, xylose and arabinose, to xylitol and arabinitol, can be modeled based on the conversion of glucose to sorbitol. The hydrogenation of the five carbon sugars to the sugar alcohols occurs

with one of many active hydrogenation catalysts such as nickel, ruthenium and rhodium. The production of xylitol for use as a building block for derivatives essentially requires no technical development.

Significant amounts of hemicellulose by-products from ethanol production are rich in pentoses such as xylose and arabinose as well as other sugars. Xylitol, a five-carbon polyol that has gained acceptance as a natural food sweetener, can be made from pure xylose by chemical hydrogenation, but production from a mixed pentose stream such as that found in hemicellulose is difficult and expensive due to separation issues. zuChem Inc., a producer of glycochemicals and specialized sugars for the food ingredients has been awarded a SBIR Phase I grant by the Department of Energy to develop a novel bioprocess for the production of xylitol from agricultural biomass (Demirjani, et al., 2007). They have developed high efficiency fermentation strains capable of converting xylose and arabinose to xylitol by combining a variety of microbial genes and pathways. The fermentation is carried out in an engineered *E. coli* which also utilizes the other sugars in the mixture as carbon sources, thus producing xylitol with no other competing polyol by-products produced. The increasing demand for xylitol volume should provide a unique match as a co-product made alongside ethanol and other fuels produced from a biorefinery.

Itaconic Acid: Itaconic acid is a C5 dicarboxylic acid, also known as methyl succinic acid and has the potential to be a key building block for deriving both commodity and specialty chemicals. The basic chemistry of itaconic acid is similar to that of the petrochemicals derived maleic acid/anhydride. The chemistry of itaconic acid to the derivatives is shown in Figure 51.

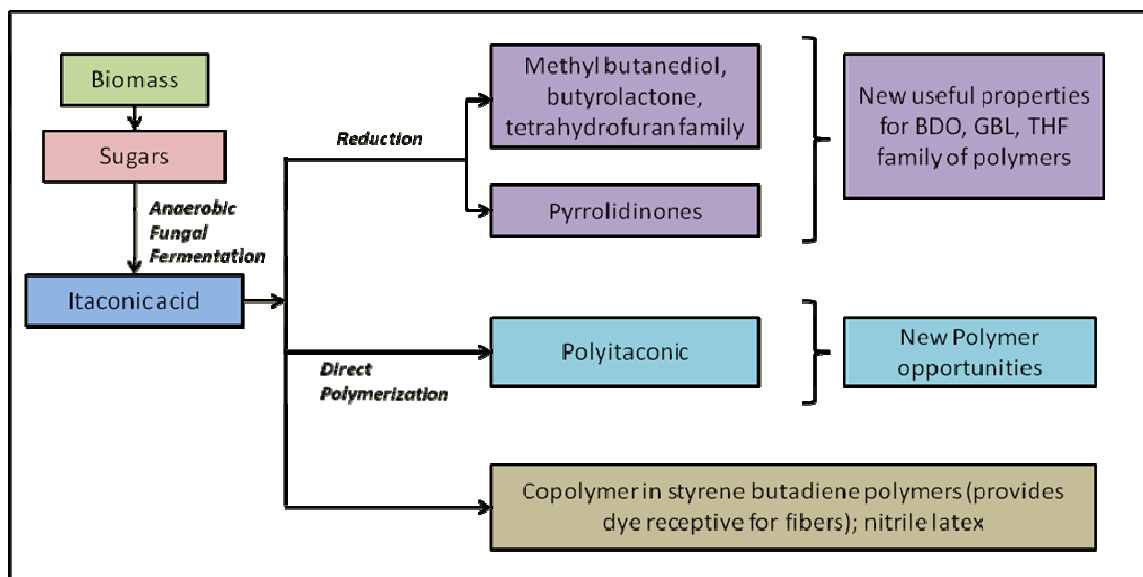


Figure 51 Production and Derivatives of Itaconic Acid (Werpy et al., 2004)

Itaconic acid is currently produced via fungal fermentation and is used primarily as a specialty monomer. The major applications include the use as a copolymer with acrylic acid and in styrene-butadiene systems. The major technical hurdles for the development of itaconic acid as a building block for commodity chemicals include the development of very low cost fermentation routes. The primary elements of improved fermentation include increasing the

fermentation rate, improving the final titer and potentially increasing the yield from sugar. There could also be some cost advantages associated with an organism that could utilize both C5 and C6 sugars.

Six-Carbon Compounds

Sorbitol: Sorbitol is produced by the hydrogenation of glucose (Werpy et al., 2004). The production of sorbitol is practiced commercially by several companies and has a current production volume on the order of 200 million pounds annually. The commercial processes for sorbitol production are based on batch technology and Raney nickel is used as the catalyst. The batch production ensures complete conversion of glucose.

The technical development possible for sorbitol manufacture can be in the conversion of glucose to sorbitol in a continuous process instead of a batch process. Engelhard (now a BASF-owned concern) has demonstrated that the continuous production of sorbitol from glucose can be done continuously using a ruthenium-on-carbon catalyst (Werpy, 2004). The yields demonstrated were near 99 percent with very high weight hourly space velocity.

Derivatives of sorbitol include isosorbide, propylene glycol, ethylene glycol, glycerol, lactic acid, anhydrosugars and branched polysaccharides (Werpy, 2004). The derivatives and their uses are described in the Figure 52.

Figure 52 Production and Derivatives of Sorbitol (Werpy et al., 2004).

2,5-Furandicarboxylic Acid: FDCA is a member of the furan family, and is formed by an oxidative dehydration of glucose (Werpy, 2004). The process has been reported to proceed using oxygen, or electrochemistry. The conversion can also be carried out by oxidation of 5-hydroxymethylfurfural, which is an intermediate in the conversion of 6-carbon sugars into levulinic acid. Some of the potential utility of FDCA are shown in Figure 53.

FDCA resembles and can act as a replacement for terephthalic acid, a widely used component in various polyesters, such as polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) (Werpy et al., 2004). PET has a market size approaching 4 billion lb/yr, and PBT is almost a billion lb/yr. The market value of PET polymers varies depending on the application, but is in the range of \$1.00 – 3.00/lb for uses as films and thermoplastic engineering polymers. PET and PBT are manufactured industrially from terephthalic acid, which, in turn, is manufactured from toluene (Wells, 1999). Toluene is obtained industrially from the catalytic reforming of petroleum or from coal. Thus, FDCA derived from biomass can replace the present market for petroleum-based PET and PBT.

FDCA derivatives can be used for the production of new polyester, and their combination with FDCA would lead to a new family of completely biomass-derived products. New nylons can be obtained from FDCA, either through reaction of FDCA with diamines, or through the conversion of FDCA to 2,5-bis(aminomethyl)-tetrahydrofuran. The nylons have a market of almost 9 billion lb/yr, with product values between \$0.85 and 2.20/lb, depending on the application.

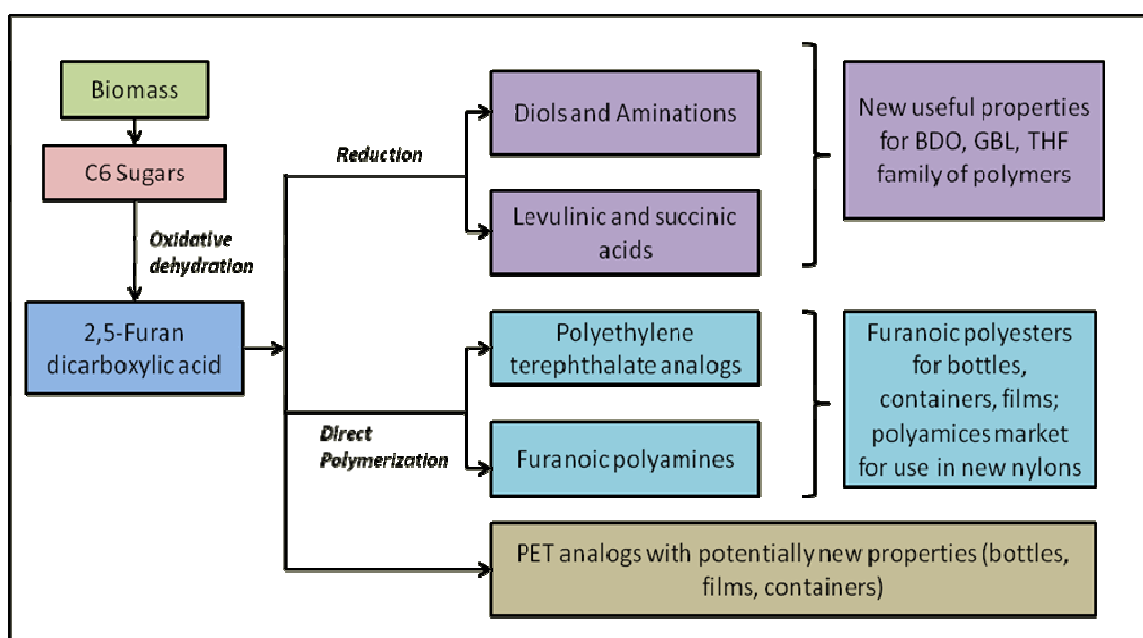


Figure 53 Production and Derivatives of 2,5-FDCA (Werpy et al., 2004)

Cellulose Acetate: Research has been reported using waste cellulose from corn fiber, rice hulls and wheat straw to produce cellulose acetate. Conversions of cellulose to cellulose acetate have been 35-40% in a laboratory study. The incentive to pursue this line of work was the price of cellulose acetate, approximately \$2.00 per pound, a more valuable product than ethanol (Ondrey, 2007c).

Vegetable Oil Based Chemicals

Soybean oil can be used to manufacture molecules with multiple hydroxyl groups, known as polyols (Tullo, 2007c). Polyols can be reacted with isocyanates to make polyurethanes. Soybean oil can also be introduced in unsaturated polyester resins to make composite parts.

Soybean-oil-based polyols have the potential to replace petrochemical-based polyols derived from propylene oxide in polyurethane formulations (Tullo, 2007c). The annual market for conventional polyols is 3 billion pounds in the U.S. and 9 billion pounds globally.

Dow Chemicals, world's largest manufacturer of petrochemical polyols, also has started the manufacture of soy-based polyols. Dow uses the following process for the manufacture of polyols. The transesterification of triglycerides give methyl esters which are then hydroformylated to add aldehyde groups to unsaturated bonds. This is followed by a hydrogenation step which converts the aldehyde group to alcohols. The resultant molecule is used as a monomer with polyether polyols to build a new polyol. Dow plans to implement the technology at their Houston plant. Urethane Soy Systems manufactures soy based polyols at Volga, South Dakota with a capacity of 75 million pounds per year and supplies them to Lear Corp., manufacturer of car seats for Ford Motor Company. The company uses two processes for the manufacture of polyols; an auto-oxidation process replacing unsaturated bonds in the triglycerides with hydroxyl groups and a transesterification process where rearranged chains of triglycerides are reacted with alcohols. Bio-Based Technologies supply soy polyols to Universal Textile Technologies for the manufacture of carpet backing and artificial turf. Johnson Controls uses their polyols to make 5% replaced foam automotive seats. The company has worked with BASF and Bayer Material Science for the conventional polyurethanes and now manufactures the polyols by oxidizing unsaturated bonds of triglycerides. The company has three families of products with 96, 70 and 60% of biobased content.

Soybean oil can be epoxidized by a standard epoxidation reaction (Wool, 2005). The epoxidized soybean oil can then be reacted with acrylic acid to form acrylated epoxidized soybean oil (AESO). The acrylated epoxidized triglycerides can be used as alternative plasticizers in polyvinyl chloride as a replacement for phthalates.

Aydogan et al., 2006 gives a method for the potential of using dense (sub/supercritical) CO₂ in the reaction medium for the addition of functional groups to soybean oil triglycerides (SOT) for the synthesis of rigid polymers. The reaction of SOT with KMnO₄ in the presence of water and dense CO₂ is presented in this paper. Dense CO₂ is utilized to bring the soybean oil and aqueous KMnO₄ solution into contact. Experiments are conducted to study the effects of temperature, pressure, NaHCO₃ addition, and KMnO₄ amount on the conversion (depletion by bond opening) of soybean-triglyceride double bonds (STDB). The highest STDB conversions, about 40%, are obtained at the near-critical conditions of CO₂. The addition of NaHCO₃ enhances the conversion; one mole of NaHCO₃ per mole of KMnO₄ gives the highest benefit. Increasing KMnO₄ up to 10% increases the conversion of STDB.

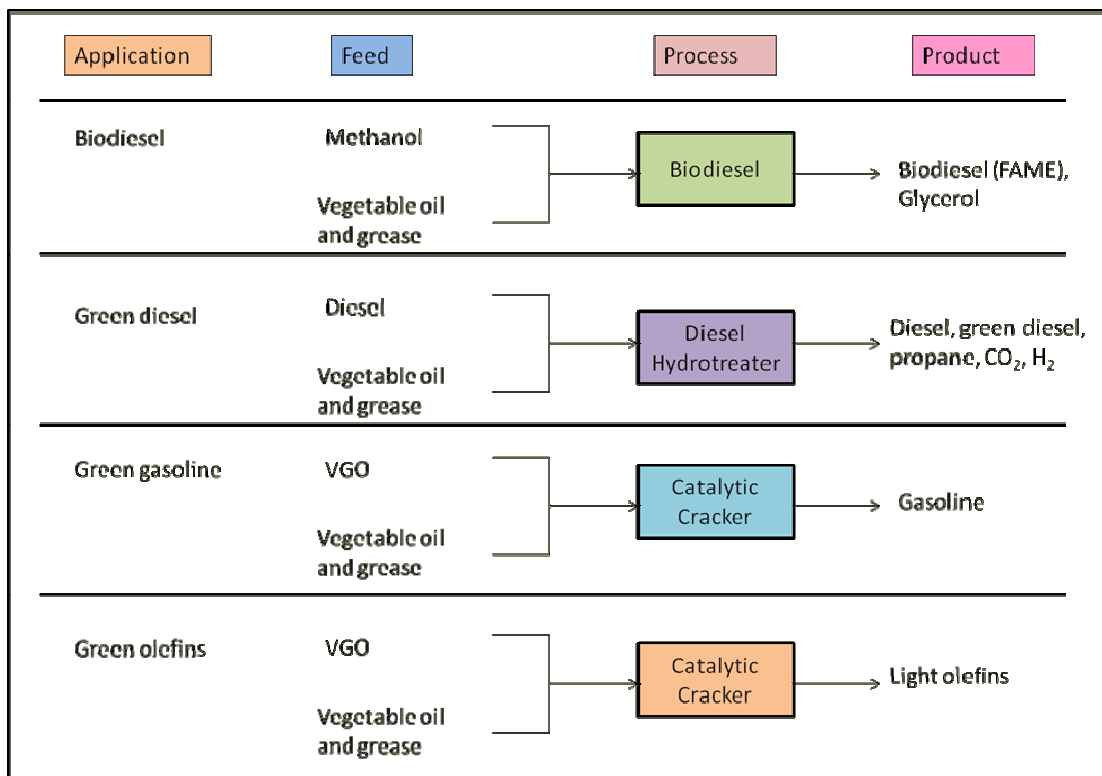


Figure 54 Processing Routes for Vegetable Oils and Grease (Holmgren et al., 2007)

Holmgren et al., 2007 discusses the uses of vegetable oils as feedstock for refineries. Four processes are outlined as shown in Figure 54. The first process is the production of fatty acid methyl esters by transesterification process. The second process is the UOP/Eni Renewable Diesel Process that processes vegetable oils combined with the crude diesel through hydroprocessing unit. The third and fourth processes involve the catalytic cracking of pretreated vegetable oil mixed with virgin gas oil (VGO) to produce gasoline, olefins, light cycle oil and clarified slurry oil. Petrobras has a comparable H-Bio process where vegetable oils can also be used directly with petroleum diesel fractions (Costa, 2007).

Incorporating Processes for Chemicals from Biomass in Chemical Production Complexes

The vision is the development of new industries in the region that are based on renewable resources which supply the products and services of the current ones. It includes transitioning existing plants to ones using biomass feedstocks that require nonrenewable resource supplements. The chemical complexes in the Gulf Coast are uniquely positioned to take advantage of bio-derived feedstocks. There is strong agricultural industry in the region, and the Mississippi River provides deep-water ports to ensure continuous supply of bio-feedstocks throughout the year.

Using the Chemical Complex Analysis System, the initial evaluation is the introduction of plants producing ethanol to go into ethylene product chain and plants using glycerin to go into the propylene chain. This evaluation includes algae which have the potential for being an

important source of oil and carbohydrates for chemicals with yields of 15, 000 gallons of oil/acre.

The analysis will be extended to production facilities that use biomass containing cellulose, hemicellulose, lignin, fats and lipids and proteins as raw materials. For biomass containing mainly cellulose, hemicellulose and lignin, processing plants will employ various pretreatment procedures to separate the components. Steam hydrolysis breaks some of the bonds in cellulose, hemicellulose and lignin. Acid hydrolysis solubilizes the hemicellulose by depolymerizing hemicellulose to 5-carbon sugars such as pentose, xylose, and arabinose. Plants will incorporate separations processes for extracting the chemicals from 5-carbon sugars. The cellulose and lignin stream is then subjected to enzymatic hydrolysis where cellulose is depolymerized to 6-carbon glucose and other 6-carbon polymers which separate the cellulose stream from lignin. Three separate streams are obtained from biomass. Fermentation reactors will be included to have the cellulose and hemicellulose monomers, glucose and pentose undergo fermentation to yield chemicals like ethanol, succinic acid, butanol, xylitol, arabinitol, itaconic acid and sorbitol. The lignin stream is rich in phenolic compounds which can be separated, and the stream can be dried to form char and used in a processing facility for gasification to produce syngas. A production plant for pyrolysis or thermal decomposition of biomass generates a complex liquid mixture and a solid similar to powdered coal. The liquid can be used to manufacture phenol-formaldehyde resins. A processing plant for direct chemical conversion of biomass, such as hydrogenation of lignin will yield phenols, and synthesis gas can be fermented to ethanol.

Production facilities with biomass feeds containing oils, lipids and fats can be transesterified to produce fatty acid methyl and ethyl esters and glycerol. The glycerol from transesterification can be converted to propylene glycol, 1,3-propanediol and other compounds in plants that can replace ones using natural-gas-based chemicals. Production plants using vegetable oils, particularly soybean oil, as feedstocks will be evaluated for the production of various polyols with a potential to replace propylene-oxide-based chemicals. The acrylated epoxidized triglycerides from soy bean oil can be used as alternative plasticizers in polyvinyl chloride as a replacement for phthalates. Vegetable oils can be directly blended in petroleum diesel fractions and catalytic cracking of these fractions produce biomass-derived fuels for chemicals.

An economic evaluation was made by Wright and Brown, 2007 for five plants each having a capacity of 150 million gallons of gasoline equivalent per year producing the following products: grain ethanol, cellulosic ethanol, methanol, hydrogen, and Fischer-Tropsch liquids. They concluded that advanced biofuels plants have a capital cost of the order at five times that of a comparable sized starch ethanol plant. The ranking for capital and operating cost are the same with hydrogen being the least expensive followed by methanol, cellulosic ethanol and Fischer-Tropsch liquids. It was concluded that neither biochemical nor thermochemical have a clear advantage in capital or operating costs for the production of advanced biofuels.

Banholzer et. al, 2008 evaluates the impact of biofuels on the chemical industry. They evaluate a bio-based ethylene production and discuss various aspects in setting up such a plant. The capital cost for top 50 chemical companies combined is \$39.7 billion, which, in order of increasing risk, is invested in projects involving extension of existing facilities, in new facilities

serving an existing market based on mature technology, in new facilities serving an existing market based on new technology and in new facilities serving a new market based on new technology. An ethanol-to-ethylene plant is considered to fall in the second and third category, as the process steps are known but a fully integrated combination of ethanol production and ethylene production are yet to be constructed.

Banholzer et. al, 2008, discusses a scenario analysis out to 2020 involving assumptions on capital expenditure and predicting the resulting market penetration of bio-derived chemicals. The analysis uses the following assumptions:

- The capital budget of top 50 companies grows at 5% per year
- The proportion of that budget spent on bio-derived ethylene grows linearly from near-zero in 2007 to 10% in 2020
- The cost of these new integrated facilities is \$2 million per Gg of capacity
- Advances in biotechnology allow the capital cost to remain flat over the time-period of 2007-2020

The predicted market penetration of bio-derived ethylene under the above assumptions is concluded to be around 12% in 2020, as shown in Figure 55.

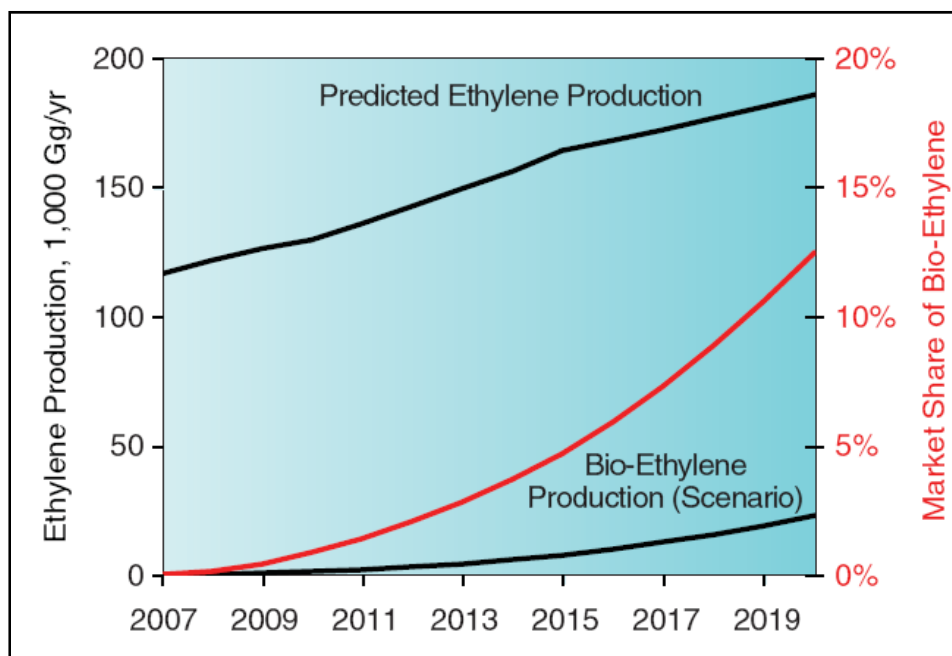


Figure 55 Scenario analysis of the potential market penetration of bio-derived ethylene by 2020 (Banholzer et. al, 2008)

The land and capital required to replace chemical ethylene base is given in Figure 56. The integrated ethanol-to-ethylene plant's capital requirements are estimates with $\pm 20\%$ error bars for capital and $\pm 10\%$ error bars for land requirements. U.S. cropland equivalent required for the producing the feedstock is shown in percentage for comparison. Combined cane/bagasse and corn/cob cellulosic ethanol plants would require less land but more capital investments. Standalone cellulosic ethanol plants would require significantly more capital than other methods analyzed.

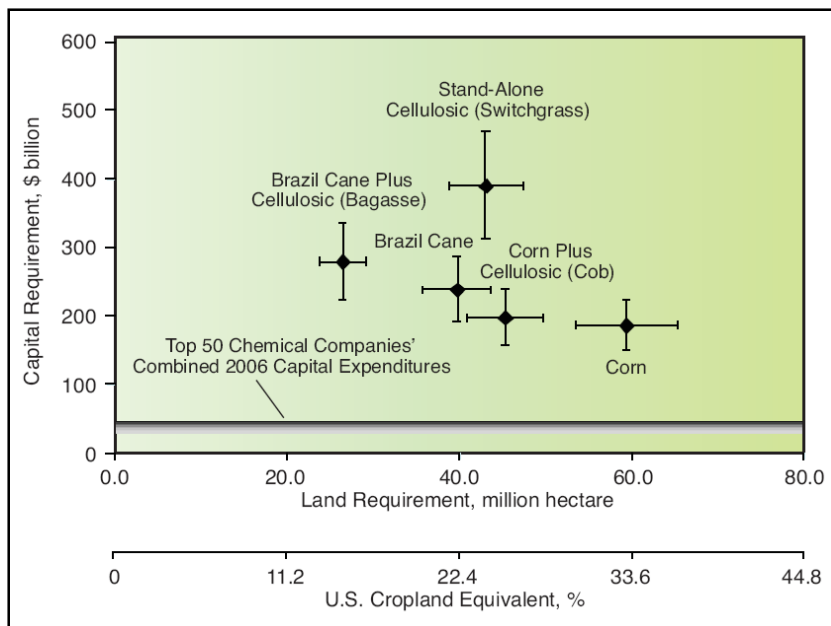


Figure 56 Estimation of capital and land requirements to replace existing chemical-derived ethylene base (Banholzer et. al, 2008).

The variable cost in a biomass-based industry includes the cost of feedstock. The feedstocks in a biomass-based industry is varied and the cost can be considered as a function the energy content of the feedstock. The prices for different feedstocks and products are based on different units. Banholzer et. al, 2008 developed a chart comparing feedstocks and products on a \$/GJ basis as shown in Figure 57.

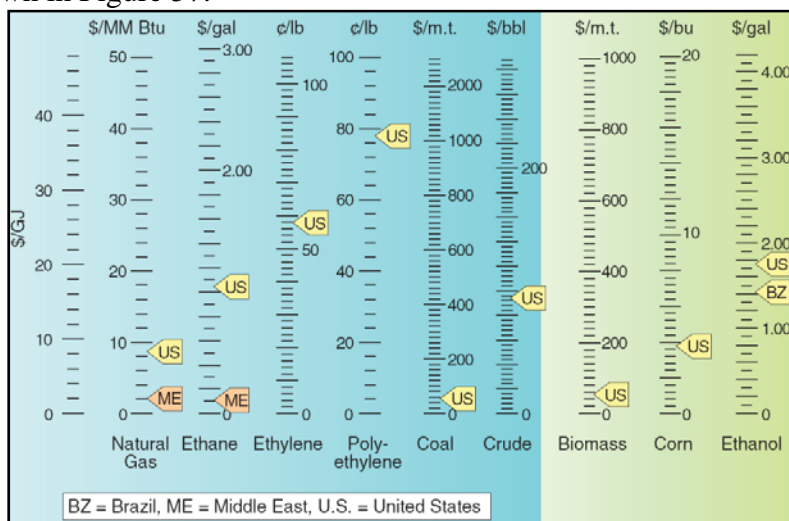


Figure 57 Relative price in 2007 per unit energy of various feedstocks and products, quoted in their traditional units and calibrated to \$/GJ (Banholzer et. al, 2008)

Banholzer et. al concluded that there exists a trade-off between variable and capital costs. As an example, the capital cost versus variable cost of olefin production using various technologies is given in Figure 58. The diagonal lines represent approximate economic-cost-of-production equivalency curves. Figure 58 also shows the effect in olefin production based on a

hypothetical carbon tax ranging from \$25/m.t. to \$125/m.t. carbon dioxide produced in the process. The evaluation did not consider a carbon tax for processes that are biomass feedstock based, but a tax for processes based on non-renewable feedstock sources including natural gas.

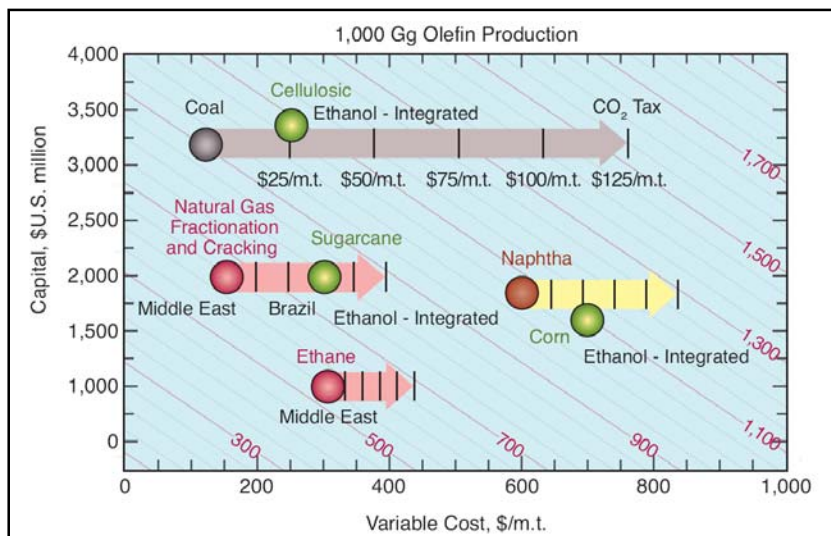


Figure 58: Contour plot of production cost plus return on investment as a function of capital and variable costs (based on 1000 Gg/yr of olefin production) (Banholzer et. al, 2008).

In Figure 59, production units proposed for the biomass based chemical complex are shown. The boxes in green give the feedstock, the orange boxes give the processes and blue and red give the products. This complex has methanol from syngas being used in transesterification of vegetable oils. A process for carbon nanotubes based on the conceptual design of Agboola, 2005 is included which will use carbon monoxide from biomass gasification,

In Figure 60 there is an illustration of incorporating processes using biomass as feedstock in the chemical production complex of existing plants. The complex of existing plants is called the Base Case. The result of combining the new plants with the Base Case gives a superstructure of plants that can be used to determine the optimal configuration of plants. The objective function used for the optimization is the triple bottom line that incorporates economic, environmental and sustainable costs. A description of the multicriteria optimization using the triple bottom line is shown in Figure 61.

The analysis used in the Chemical Complex Analysis System incorporates the description of the existing plants in the Base Case that includes the material and energy balance equations, rate equations and equilibrium relations, plant capacities, availability of raw materials and demand for products. This same information is being developed for the processes using biomass feedstock. Processes that utilize carbon dioxide will be incorporated and extended from the results obtained by Xu, 2004, and a process for carbon nanotubes will be included based on the conceptual design of Agboola, 2005 which can use carbon monoxide from biomass syngas production.

Triple bottom line costs are being evaluated and include economic and environmental costs and sustainable credits and costs. These are to be used in the multicriteria, mixed integer

nonlinear programming problem which will use global and local solvers to determine the Pareto optimal solutions. Monte Carlo Analysis is to be used to determine sensitivity of the optimal solution to the parameters in the optimization problem.

Consideration for extensions include plants in the Gulf Coast Region (Texas, Louisiana, Mississippi, Alabama) and demonstration that the methodology can be applied to other chemical complexes of the world.

In summary, in Figure 62 some of the existing chemicals are shown that are produced from biomass based feedstock. For example, HDPE is produced from ethanol-based ethylene and propylene glycol is produced from glycerol. In Figure 63 some new chemicals are shown that are produced from biomass. For example, The Ford Motor Company plans to use soy polyurethane foams in their car seats.

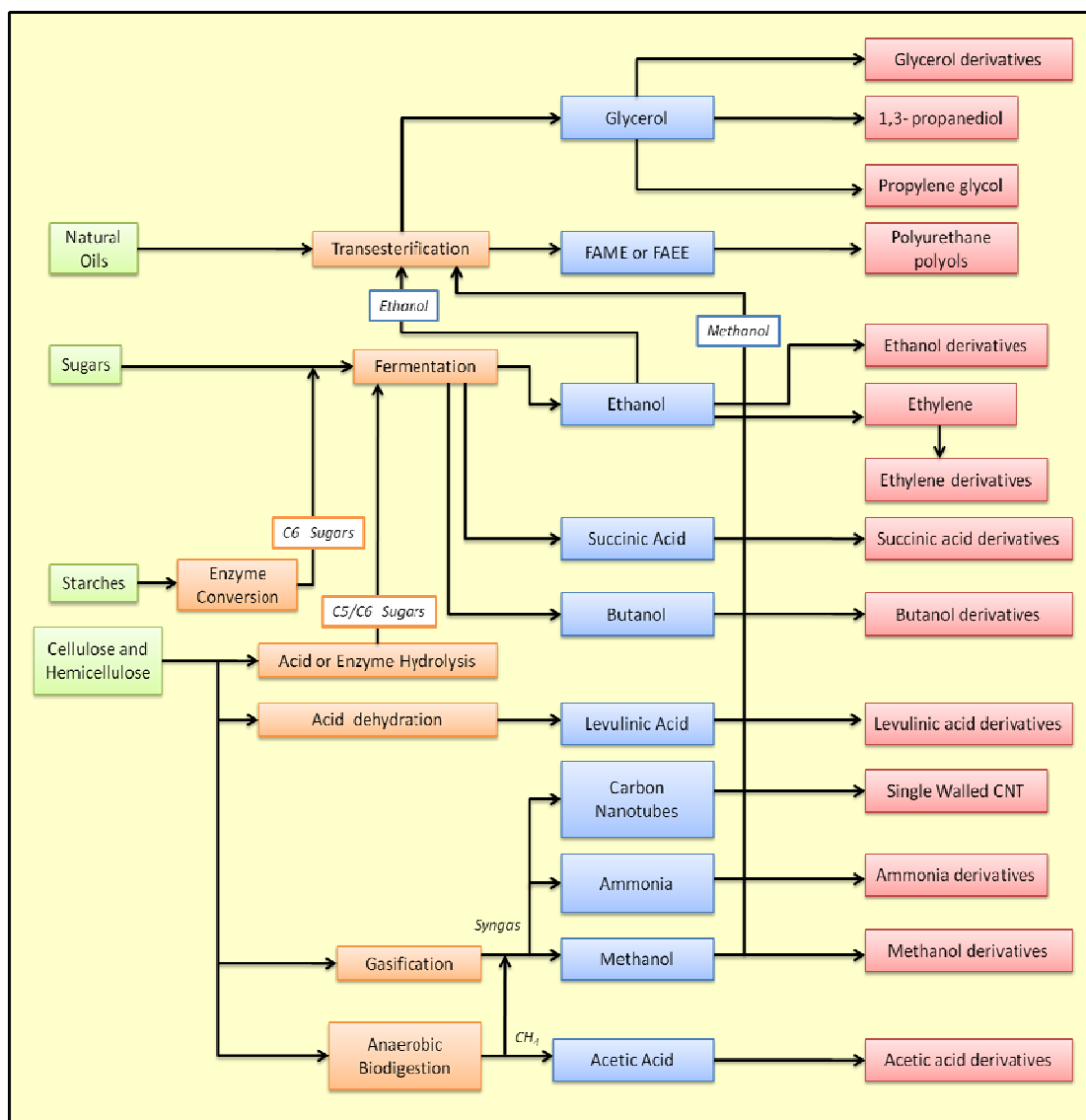


Figure 59 Proposed Biomass Based Complex Extension with Single-Wall Carbon Nanotube Production

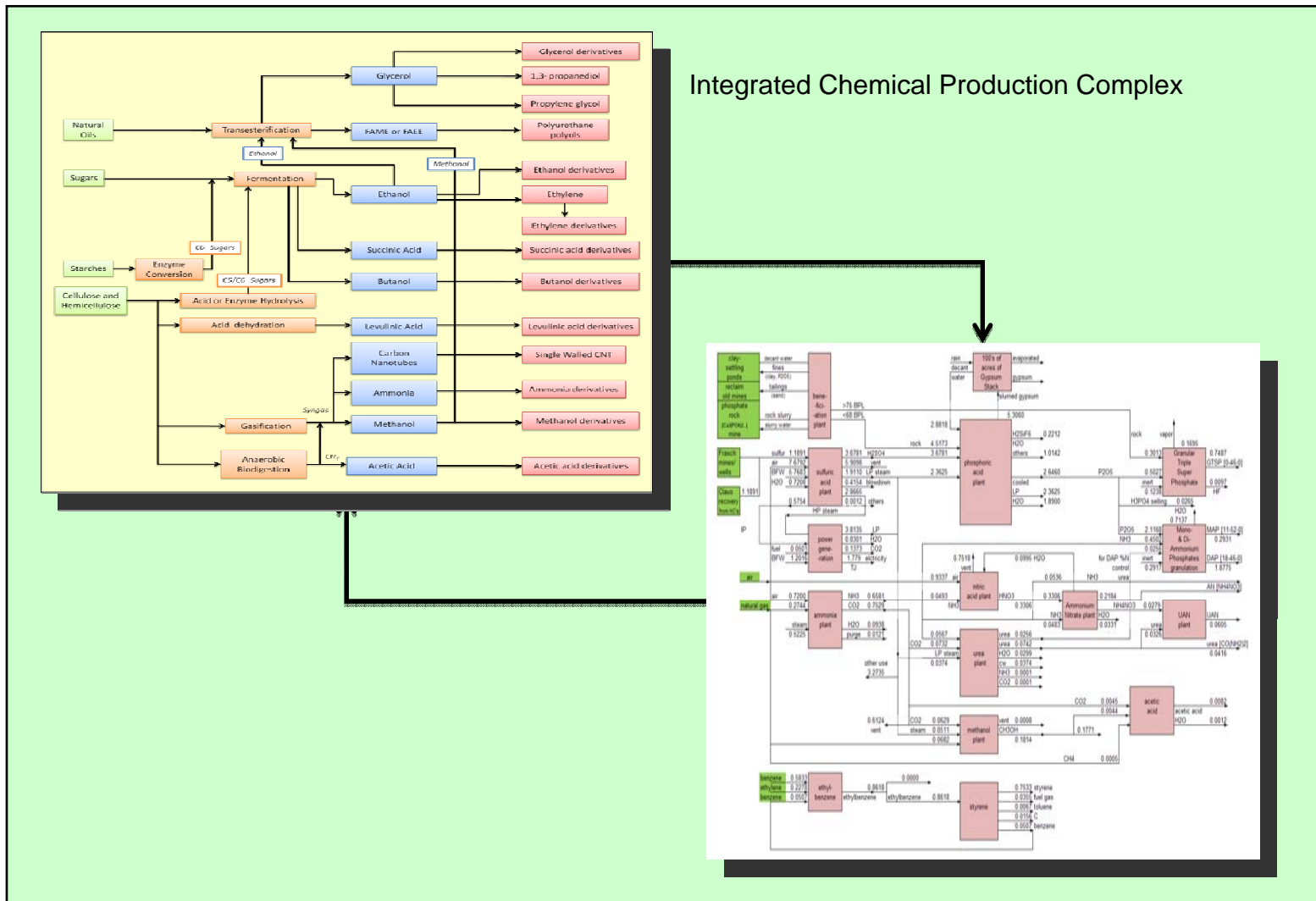


Figure 60 Illustration of Incorporating Processes Using Biomass as Feedstock into the Chemical Production Complex (Base Case of Existing Plants)

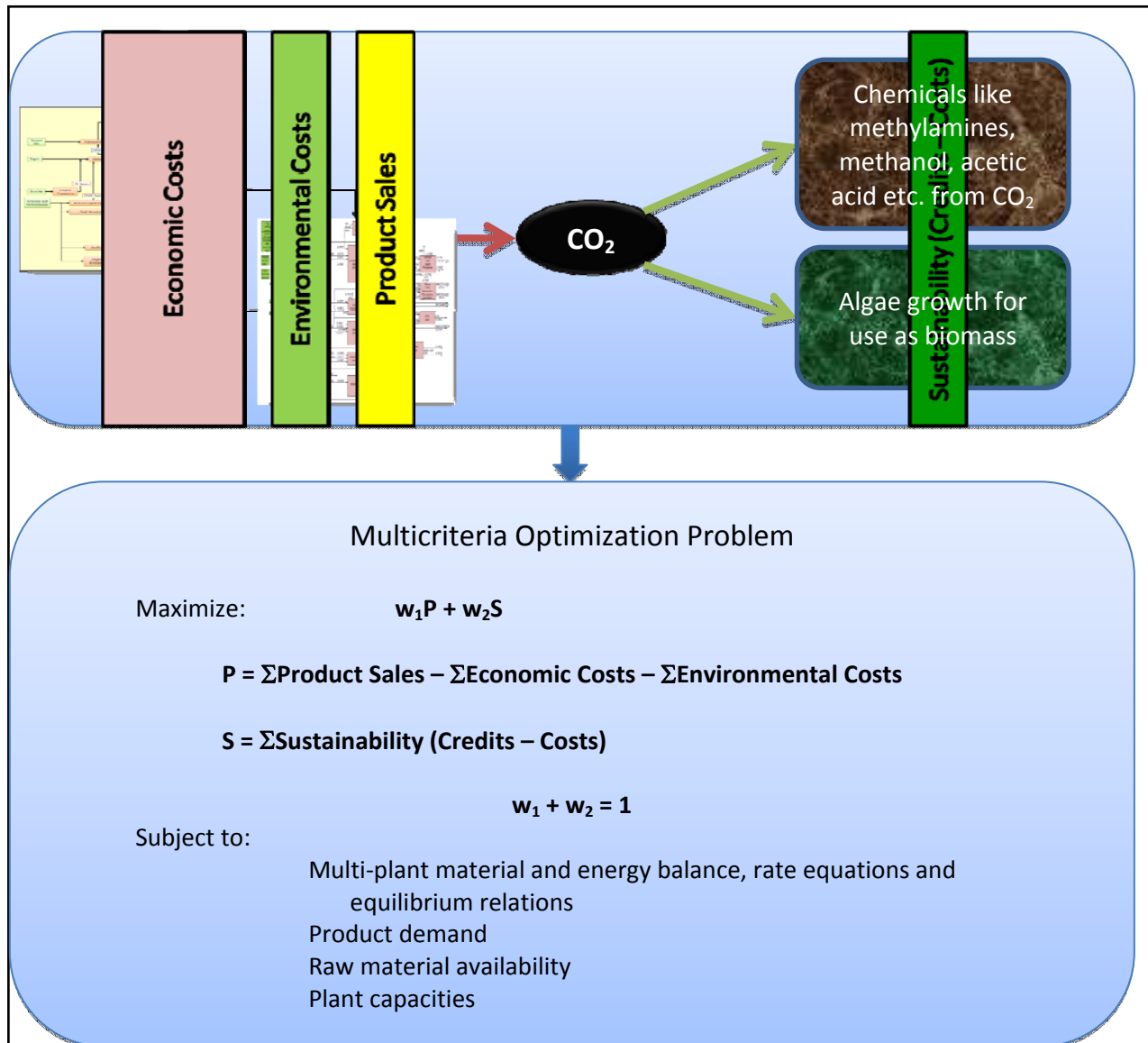


Figure 61 Description of Multicriteria Optimization using the Triple Bottom Line

Existing Products



HDPE

Tetrahydrofuran (THF)



Propylene Glycol

These are currently manufactured from petroleum and natural gas as feedstock.

These can be manufactured from biomass based feedstock.



Butanediol



Cellulose Acetate



PVA



Glycerol

Figure 62 Existing Chemicals Produced from Biomass Based Feedstock. For example, HDPE is produced from ethanol based ethylene and propylene glycol is produced from glycerol.

New Products from Biomass



Zemea™

Pro-Cote®



Figure 63 New Chemicals from Biomass

Chemical Complex Analysis System

The chemical production complex shown in Figure 2 is representative of current operations and practices in the chemical industry and is called the base case of the existing plants. This description of the chemical production complex was used in research on carbon dioxide utilization. It will be used to demonstrate the integration of new processes using biomass feedstock and converting processes based on nonrenewable resources to ones based on renewable resources using the Chemical Complex Analysis System.

The Chemical Complex Analysis System was developed at the LSU Minerals Processing Research Institute to determine the best configuration of plants in a chemical complex based on economic, energy, environmental and sustainable costs. The system structure is shown in Figure 64. 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. These equations are entered through a graphical user interface and stored in the database to be shared with the other components of the system.

The objective function is entered as an equation associated with each process with related information for prices and economic, energy, environmental and sustainable costs that are used in the evaluation of the Total Cost Assessment (TCA) for the complex. The TCA includes the total profit for the complex that is a function of the economic, energy, environmental and sustainable costs and income from sales of products. Then the information is provided to the mixed-integer nonlinear programming solver to determine 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) which is similar to the TRACI system of EPA.

Figure 64 Program Structure for the Chemical Complex Analysis System

References

Agboola, Adedeji E., 2005b, *Development and Model Formulation of Scalable Carbon Nanotube Processes: HiPCO and CoMoCAT Process Models*, M. S. Thesis, Louisiana State University, Baton Rouge, LA.

Aden A., Ruth M., Ibsen K., Jechura J., Neeves K., Sheehan J., Wallace B., 2002, "Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover", NREL/TP-510-32438, National Renewable Energy Laboratory, Golden, CO, (June 2002)

Aiello-Mazzarri C., G. Coward-Kelly, F. K. Agbogbo and M. T. Holtzaple, 2005, "Conversion of Municipal Solid Waste into Carboxylic Acids by Anaerobic Countercurrent Fermentation", *Applied Biochemistry and Biotechnology*, Humana Press Inc., Vol. 127, Pg. 79-93.

Arakawa, H., et al., 2001, "Catalyst Research of Relevance to Carbon Management: Progress, Challenges and Opportunities", *Chem. Rev.*, Vol. 101, p. 953-996.

Arnaud, C., "Algae pump out Hydrocarbon Biofuels", *Chemical & Engineering News*, p. 45, September 1, 2008.

Atkinson, B. and F. Mavituna, 1983, *Biochemical Engineering and Biotechnology Handbook*, the Nature Press, MacMillan Publishers, Surrey, England.

Austin G.T., 1984, *Shreve's Chemical Process Industries*, fifth edition, ISBN 0070571473, McGraw-Hill Book Company, USA.

Aydogan S., S. Kusefoglul, U. Akman, O. Hortacsu, 2006, "Double-bond depletion of soybean oil triglycerides with KMnO_4/H_2 in dense carbon dioxide", *Korean Journal of Chemical Engineering*, Vol. 23, Issue 5, Pg. 704-713.

Bain, R., 2007, *Biomass Gasification and Pyrolysis: Overview and NREL Research*, Twelfth New Industrial Chemistry and Engineering Conference on Biobased Feedstocks, Council for Chemical Research, Argonne National Laboratory, Chicago, IL (June 11-13, 2007).

BASF, 2007, "Ecovio®, in harmony with nature", http://www2.basf.de/basf2/html/plastics/images/pdfs/engl/polymere/Ecovio_Flyer_e.pdf, (Accessed September 11, 2007)

Bourne, Jr., J.K., 2007, "Green Dreams", *National Geographic Magazine*, October, 2007, <http://magma.nationalgeographic.com/ngm/2007-10/biofuels/biofuels.html>, accessed 10/10/2007.

Byers, Paula, 2006, Louisiana Department of Economic Development, Private Communication

Cabezas, H., J. C. Bare, and S. K. Mallick, 1997, "Pollution Prevention with Chemical Process Simulators: The General Waste Reduction Algorithm," *Computers and Chemical Engineering*, Vol. 21, Supp S305-310.

Cameron D.C., Koutsky J.A., 1994, "Conversion of Glycerol from SoyDiesel Production to 1,3-Propanediol", Final Report prepared for National Biodiesel Development Board, Department of Chemical Engineering, UW-Madison, Madison, WI.

C&E News, 2006, "Marathon sets ethanol venture", *Chemical & Engineering News*, Volume 84, Issue 29, pg. 21, July, 2006.

C&E News, 2007a, "ConocoPhillips funds Biofuel research", *Chemical & Engineering News*, Volume 85, Issue 18, pg. 24, April 16, 2007

C&E News, 2007b, "Dow to Make Polyethylene from Sugar in Brazil," *Chemical & Engineering News*, Vol. 85, No. 30, p. 17, July 23, 2007.

C&E News, 2007c, "Solvay will Produce Bio-Polyvinyl Chloride," *Chemical & Engineering News*, Vol. 85, No. 52, p. 20, December 24, 2007.

CEP, 2007, "\$100-Million Plant is First to Produce Propanediol from Corn Sugar," *Chemical Engineering Progress*, p. 10 (January, 2007).

Cheryan, M., 2007, "Separations for the Biobased Era," Twelfth New Industrial Chemistry and Engineering Conference on Biobased Feedstocks, Council for Chemical Research, Argonne National Laboratory, Chicago, IL (June 11-13, 2007)

Cockrem, M., 2007 "Opportunities for Industrial Chemicals from Biobased Feedstocks," Twelfth New Industrial Chemistry and Engineering Conference on Biobased Feedstocks, Council for Chemical Research, Argonne National Laboratory, Chicago, IL (June 11-13, 2007)

Creutz, C. and Fujita, E., 2000, "Carbon Dioxide as a Feedstock", *Carbon Management: Implications for R&D in the Chemical Sciences and Technology: A Workshop Report to the Chemical Sciences Roundtable*, The National Academies Press, Washington, D.C.

Crocker M., C. Crofchek, 2006, "Biomass Conversion to Liquid Fuels and Chemicals", University of Kentucky's Center for Applied Energy Research (CAER), Vol. 17, No. 6, pg. 1-3.

D'Aquino R., 2007, "Cellulosic Ethanol – Tomorrow's Sustainable Energy Source", *Chemical Engineering Progress*, March 2007.

Dasari, M. A., P.-P. Kiatsimkul, W. R. Sutterlin and G. J. Suppes, 2005, "Low-Pressure Hydrogenolysis of Glycerol to Propylene G," *Applied Catalysis, A: General*, Vol. 281, p. 225-231.

de Hope, C. F., et al. 2006, *Biomass Energy Resources in Louisiana*, Research Information Sheet 102, LSU Agricultural Center, Baton Rouge, LA.

Demirjian, D., R. D. Woodyer, M. Racine, and B. C. Saha, 2007, "Production of Xylitol from Agricultural Hemicellulosic Biomass," Paper No. 574d, Salt Lake City AIChE Annual Meeting, November 4-8, 2007

DOE, 2007, "DOE Selects Six Cellulosic Ethanol Plants for Up to \$385 Million in Federal Funding", <http://www.energy.gov/print/4827.htm> , (February 28, 2007) accessed 10/2/07.

ERS/USDA, 2006, "Available Ethanol Reshapes the Corn Market," <http://www.ers.usda.gov/AmberWaves/April06/Features/Ethanol.htm> (accessed May 24, 2006).

Fukuda H., Kondo A. and Noda H., 2001 "Biodiesel Production by the Transesterification of Oils", *Journal of Bioscience and Bioengineering*, Elsevier, Vol. 92, Issue 5, Pg. 405-416.

Granada, Cesar, 2007, "MixAlco Process," *Alternative Energy 2007, Seizing Opportunity in an Expanding Energy Marketplace*, Center for Energy Studies Conference, Louisiana State University, Baton Rouge, LA (April 25, 2007).

Hayes D.J., S. Fitzpatrick, M.H.B. Hayes, J.R.H. Ross, 2006, "The Biofine Process – Production of Levulinic acid, Furfural and Formic Acid from Lignocellulosic Feedstock", *Biorefineries – Industrial Processes and Products*, Vol. 1, ISBN 3-527-31027-4, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, Pg. 139-164

Hertwig, Thomas A., 2004, IMC Phosphate, Uncle Sam, LA, Private Communication.

Hertwig, Thomas A., 2006, IMC Phosphate, Uncle Sam, LA, Private Communication.

Hess, G., 2006, "Push for Biofuels Seen in Farm Bill," *Chemical & Engineering News*, Vol. 84, Issue 26, p. 9, June 26, 2006.

Hitchings, M. A., 2007, "Algae: the Next Generation of Biofuels," *Fuel*, Fourth Quarter 2007, Hart Energy Publishing, Houston, TX.

Holmgren J., C. Gosling, K. Couch, T. Kalnes, T. Marker, M. McCall and R. Marinangeli, 2007, "Refining Biofeedstock Innovations," *Petroleum Technology Quarterly*, Third Quarter, Vol 12, No. 4, p. 119-124.

Indala, Sudheer, 2004, *Development and Integration of New Processes Consuming Carbon Dioxide in Multi-Plant Chemical Production Complexes*, M. S. Thesis, Louisiana State University, Baton Rouge, LA.

Johnson, J. 2007, "Farm Energy," *Chemical & Engineering News*, p. 50 (May 7, 2007).

Johnson, J. 2007, "EPA Boost Ethanol," *Chemical & Engineering News*, p. 27 (April 30, 2007).

Kamm B., Kamm M., Gruber P.R., Kromus S., 2006, "Biorefinery Systems – An Overview", *Biorefineries – Industrial Processes and Products*, Vol. 1, ISBN 3-527-31027-4, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, Pg. 3-33.

Karinen R.S., Krause A.O.I., 2006, "New Biocomponents from Glycerol", *Applied Catalysis A: General*, Elsevier, Vol. 306, pg. 128-133, June 2006.

Katzen R., Schell D.J., "Lignocellulosic Feedstock Biorefinery: History and Plant Development for Biomass Hydrolysis", *Biorefineries – Industrial Processes and Products*, Vol. 1, ISBN 3-527-31027-4, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, Pg. 129-136.

Kebanli, E. S., R. W. Pike, D. D. Culley and J. B. Frye, 1981, "Fuel Gas from Dairy Animal Wastes" *Agricultural Energy Vol. II Biomass Energy Crop Production*, ASAE Publication 4-81 (three volumes), American Society of Agricultural Engineers, P.O. Box 410, St. Joseph, MI 49085.

Klass, D. L., 1998, *Biomass for Renewable Energy, Fuels and Chemicals*, Academic Press, San Diego, CA.

LSU Ag Center, 2007: Web reference accessed 05/30/2007

<http://www2.lsuagcenter.com/Communications/agsum/agsum05/statetotals.aspx>, Louisiana State University Agricultural Research Center, Baton Rouge, Louisiana.

Ma F and Hanna M.A., 1999, "Biodiesel Production: A Review", *Bioresource Technology*, Vol. 70, p. 1-15

Marchetti, J. M., V. U. Miguel, and A. F. Errazu, 2007, "Possible Methods for Biodiesel Production," *Renewable and Sustainable Energy Reviews*, Vol. 11, p. 1300-1311.

Marinangeli, R., 2007, "Refining Biorenewables using UOP/Eni Renewable Diesel Process," Twelfth New Industrial Chemistry and Engineering Conference on Biobased Feedstocks, Council for Chemical Research, Argonne National Laboratory, Chicago, IL (June 11-13, 2007)

McCoy, M., "Biofuels Merger," *Chemical & Engineering News*, p. 11 (February 19, 2007).

McMillan J., 2007a, "Faustina plans new plant", *The Advocate*, June 21, 2007

McMillan J., 2007b, "Eastman, Faustina deal enhances La. Plant - Gasification process reportedly to offer state new industrial opportunity", *The Advocate*, July 27, 2007

Meher LC, Vidya Sagar D, Naik SN, 2006, "Technical aspects of biodiesel production by transesterification—a review", *Renewable and Sustainable Energy Review*, Vol. 10, Pg. 248-26

Mu Y., Teng H., Zhang D., Wang W., Xiu Z., 2006, "Microbial production of 1,3-propanediol by *Klebsiella pneumoniae* using crude glycerol from biodiesel preparations", *Biotechnology Letters*, Vol. 28, pg. 1755–1759.

Nexant, 2006, "Prospectus: Liquid Biofuels: Substituting for Petroleum," Nexant, Inc., White Plains NY, (December, 2006)

Ondrey, Gerald, 2003, "A Process to Make Methanol from CO₂," *Chemical Engineering*, Volume 110, No. 10, p. 17, October 2003

Ondrey, Gerald, 2004, "Getting a Handle on Greenhouse Gases," *Chemical Engineering*, Vol. 111, No. 6, p. 21.

Ondrey, Gerald, 2007a, "Propylene Glycol," *Chemical Engineering*, Vol. 114, No. 6, p. 10, June 2007.

Ondrey, Gerald, 2007b, "A Vapor-Phase Glycerin-to-PG Process Slated for its Commercial Debut," *Chemical Engineering*, Vol. 114, No. 8, p. 12, August 2007.

Ondrey, Gerald, 2007c, "Coproducts of Cellulose Acetate Promises to Improve Economics of Ethanol Production," *Chemical Engineering*, Vol. 114, No. 6, p. 12, June, 2007.

Ondrey, Gerald, 2008, "Dow and NREL join forces in a biomass gasification project," *Chemical Engineering*, p. 13, August 2008.

Paster, M., J. L. Pellegrino and T. M. Carole, 2003, "Industrial Bioproducts: Today and Tomorrow," Department of Energy Report prepared by Energetics, Inc., Columbia MD (July, 2003).

Pellegrino J.L., 2000, "Energy and Environmental Profile of the U.S. Chemical Industry" Energetics, Inc. report for U.S. Department of Energy Office of Industrial Technologies, Columbia, MD, May 2000.

Perlack, R. D., L. L. Wright, A. F. Turhollow and R. L. Graham, 2005, "Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply," Departments of Energy and Agricultural Report DOE/GO-102005-2135, Oak Ridge National Laboratory, Oak Ridge, TN (April, 2005).

Peterson, R. W., 2000, *Giants on the River*, Homesite Company, Baton Rouge, LA.

Pike, R. W., J. N-K. King E. S. Kebanli and M. D. Iliff, 1979, "Fuel Gas from Animal Waste," Fifth Chilean Chemical Engineering Congress, Valparaiso, Chile (October 18-20, 1979).

Ritter S., 2006, "Biorefineries get ready to deliver the goods", *Chemical & Engineering News*, Vol. 84, No. 34, August 21, 2006, Pg. 47.

Sheehan et. al, 1998, A Look Back at the U. S. Department of Energy's Aquatic Species Program – Biodiesel from Algae, Contract No. DE-AC36-83CH10093, National Renewable Energy Laboratory, Golden CO.

Singh, A., H. H. Lou, C. L. Yaws, J. R. Hopper and R. W. Pike, 2007, "Environmental Impact Assessment of Different Design Schemes of an Industrial Ecosystem," *Resources Conservation & Recycling*, Vol. 51, p. 294-313.

Smith, R. A., 2005, *Analysis of a Petrochemical and Chemical Industrial Zone for the Improvement of Sustainability*, M. S. Thesis, Lamar University, Beaumont, TX.

Snyder, S. W., 2007, "Overview of Biobased Feedstocks," Twelfth New Industrial Chemistry and Engineering Conference on Biobased Feedstocks, Council for Chemical Research, Argonne National Laboratory, Chicago, IL (June 11-13, 2007)

Spath, P. L., and D. C. Dayton, 2003, "Preliminary Screening – Technical and Economic Assessment of Synthesis Gas to Fuels and Chemicals with Emphasis on the Potential for Biomass-Derived Syngas," NREL/TP-510-34929, National Renewable Energy Laboratory, Golden ,CO (December, 2003).

Speight, J. G., 2002, *Chemical and Process Design Handbook*, McGraw-Hill, New York, NY.

Takahara I, Saito M, Inaba M, and Murata K, 2005, "Dehydration of ethanol into ethylene over solid acid catalysts", *Catalysis Letters*, Vol. 105, Nos. 3–4, December 2005

Teter S.A., Xu F., Nedwin G.E., Cherry J.R., 2006, "Enzymes for Biorefineries", *Biorefineries – Industrial Processes and Products*, Vol. 1, ISBN 3-527-31027-4, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, Pg. 357-382.

Thanakoses, P., A. S. Black and M. T. Holtzapple, 2003, "Fermentation of Corn Stover to Carboxylic Acids," *Biotechnology and Bioengineering*, Vol. 83, No. 2, p.191-200 (July 30, 2003).

Thrasher, L. 2006, "Mosaic Announces Non-Binding Letter of Intent for Ammonia Offtake," Press Release, Mosaic, Plymouth MN.

Tullo, A., 2007a, "Chemicals from Renewables," *Chemical & Engineering News*, , p. 14, (May 7, 2007).

Tullo, A., 2007b, "Soy Rebounds," *Chemical & Engineering News*, , p. 36, (August 20, 2007).

Tullo, A.H., 2008, "Growing Plastics", *Chemical & Engineering News*, , p. 21, (September 29, 2008).

United Nations, 1987, "Report of the World Commission on Environment and Development", 96th Plenary Meeting, 11 December 1987, <http://www.un.org/documents/ga/res/42/ares42-187.htm>.

USDA, 2007, <http://plants.usda.gov/>, Accessed October 2007.

Ushikoshi, K., et al., 1998, "A 50 kg/day class test plant for methanol synthesis from CO₂ and H₂", *Advances in Chemical Conversions for Mitigating Carbon Dioxide, Studies in Surface Science and Catalysis*, 114, p. 357-362.

Wells, G. M., 1999, *Handbook of Petrochemicals and Processes*, Sec. Ed., Ashgate Publishing Company, Brookfield, VT, USA.

Werpy, T. and G. Peterson, 2004, "Top Value Added Chemicals from Biomass: Volume 1 Results of Screening for Potential Candidates from Sugars and Synthesis Gas," National Renewable Energy Laboratory, Department of Energy (August, 2004).

Wikipedia, 2008, "Biofuel applications of botryococcene", http://en.wikipedia.org/wiki/Biofuel_applications_of_botryococcene , accessed 20 October, 2008.

Wilke T., U. Pruze, K.D. Vorlop, 2006, "Biocatalytic and Catalytic Routes for the Production of Bulk and Fine Chemicals from Renewable Resources", *Biorefineries – Industrial Processes and Products*, Vol. 1, ISBN 3-527-31027-4, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, Pg. 385-406.

Wilson, S. R., 2006, Testimony of Steven R. Wilson, Chairman and CEO, CF Industries before the Senate Committee on Energy and Natural Resources, February 16, 2006.

Wool, 2007, "Bio-based Polymers and Composites," Twelfth New Industrial Chemistry and Engineering Conference on Biobased Feedstocks, Council for Chemical Research, Argonne National Laboratory, Chicago, IL (June 11-13, 2007)

Wright, M. M. and R. C. Brown, 2007, "Comparative Economics of Biorefineries based on the Biochemical and Thermochemical Platforms," *Biofuels, Bioproducts and Biorefining*, Vol. 1, p.49-56.

Xu, A., 2004, *Chemical Production Complex Optimization, Pollution Reduction and Sustainable Development*, Ph.D. Dissertation, Louisiana State University, Baton Rouge, LA, 2004.

Zhang Z.Y., Jin B., Kelly J.M., 2007, "Production of lactic acid from renewable materials by *Rhizopus fungi*", *Biochemical Engineering Journal*, Vol. 35, pg. 251-263.

Zelder, O., 2006, "Fermentation - a versatile technology utilizing renewable resources", *Journalists and Scientists in Dialogue "Raw material change: coal, oil, gas, biomass – where does the future lie?"*, November 21/22, Ludwigshafen.