

ENCYCLOPEDIA OF ENERGY

Chemicals from Biomass

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GLOSSARY

Biomass Material generated by living organisms, typically the cellular structure of a plant or animal or chemical products generated by the organism.

Biorefinery A factory incorporating a number of processing steps, including pretreatments, separations, and catalytic and biochemical transformations, for the production of chemical and fuel products from biomass.

Carbohydrate Chemicals composed of carbon, hydrogen, and oxygen only, and typically having a hydrogen-to-oxygen ratio of 2 to 1; representatives include sugars, such as glucose or xylose, starches, and cellulose or hemicelluloses.

Catalyst An additive to a chemical reaction that increases the rate of reaction without being consumed in the reaction.

Chemurgy The philosophy of using agriculturally derived feedstocks for production of chemical products.

Fermentation The production of simple chemical products by microbial action on a complex feedstock, often a carbohydrate.

Hydrolysis A chemical reaction in which water is chemically combined into a reactant and in the process, the reactant is broken down into smaller molecules.

Hydrogenation The chemical addition of hydrogen into a molecule, usually performed in the presence of a metal catalyst; special types of hydrogenation include *hydrodeoxygenation*, in which oxygen is removed from a molecule by the reaction of hydrogen, and *hydrogenolysis*, in which a molecule is broken into smaller molecules by the reaction of hydrogen.

I. DEFINITION AND IMPACT OF CHEMICALS FROM BIOMASS

Refined processing methods and advanced technologies for biomass conversion enable low-value byproducts or waste materials to be transformed into value-added products. Such products include the same chemicals produced from petroleum that are used, for example, as plastics for car components, food additives, clothing fibers, polymers, paints, and other industrial and consumer products. Other replacement products that could be produced from biomass include different chemicals with similar or better properties. Currently, 17% of the volume of the products derived from petroleum in the United States are chemicals (see Table I). If that petroleum, used for chemical synthesis, were displaced by biomass, it would thus be available

for the energy market. In 1998 the U.S. Department of Energy stated as its goal the production of at least 10% of the basic chemical building blocks from plant-derived renewables by the year 2020 (a five-fold increase) and 50% by 2050 (a subsequent five-fold increase). The chemicals and products discussed here are capable of reducing the 17% petroleum utilization number and making a significant contribution toward meeting those goals.

The discussion on chemicals from biomass is limited to large-scale commodity products where a noticeable impact on the energy market would be made by displacing petroleum. Specialty chemical products whose limited market would have minimal impact on energy markets are not addressed, nor is the use of biomass for material products such as cellulosic fiber for paper or lignocellulosic material for construction materials. Using biomass to produce a vast array of small-market specialty chemicals based on unique biochemical structures is another part of the overall concept of a sustainable economy, but is outside the scope of this discussion. Instead, it focuses on the chemical structure of various commodity products and their fabrication from biomass. A history of the use of biomass as the basis for chemical products is included for background.

Table I. Petroleum-Derived Products in the U.S. in 2001

	Net Production, thousands of barrels per day	Percent of Net Production
Finished Motor Gasoline (total)	8,560	44.6%
Finished Aviation Gasoline (total)	22	0.1%
Jet Fuel	1,655	8.6%
Kerosene	72	0.4%
Distillate Fuel Oil	3,847	20.0%
Residual Fuel Oil	811	4.2%
Asphalt and Road Oil	519	2.7%
Petroleum Coke	437	2.3%
Chemical Products	3,283	17.1%
Liquefied Petroleum Gases (net*)	1,778	
Ethane/Ethylene	695	
Propane/Propylene	1,142	
Butane/Butylene	-5	
Isobutane/Isobutylene	-28	
Pentanes Plus	-32	
Naphtha for Petrochemicals	258	
Other Oils for Petrochemicals	312	
Special Naphthas	41	
Lubricants	153	
Waxes	18	
Still Gases	670	
Miscellaneous Products	59	
Total Net Production	19,206	

* net = products minus natural gas liquids input

source: Energy Information Administration/Petroleum Supply Annual 2001, Volume 1, Table 3

II. HISTORICAL DEVELOPMENTS

The use of biomass to meet the needs of civilization has been underway since prehistory. Several biomass chemical products can be traced to a time when neither the chemical mechanistic transformation process nor the chemical identity of the product was understood. These early products include chemicals still widely used, such as ethanol and acetic acid. A more scientific understanding of chemistry in the 19th century led to the use of biomass as a feedstock for chemical processes. However, in the 20th century, the more easily processed and readily available petroleum eventually changed the emphasis of chemical process development from carbohydrate feedstock to hydrocarbon feedstock. Through major investments by industry and government, utilization of petroleum as a chemical production feedstock has been developed to a high level and provides a wide array of materials and products. Now, that expansion of synthetic chemical products from petroleum provides the framework in which to reconsider the use of renewable biomass resources for meeting society's needs as we begin the 21st century. However, only since the 1980s has interest returned to the use of biomass and its chemical structures for the production of chemical products, so much research and development of chemical reactions and engineered processing systems remains to be done.

A. EARLY DEVELOPMENTS

The earliest biomass uses often involve food products. One of the first was ethanol, which was limited to beverage use for centuries. Ethanol's origin is lost in antiquity, but is generally thought to be an accidental development. Only with an improved understanding of chemistry in the mid-1800s was ethanol identified and its use expanded for solvent applications and as a fuel. Acetic acid -- the important component in vinegar -- is another accidental product based on fermentation of ethanol by oxidative organisms. A third fermentation product from antiquity, lactic acid, also an accidental product of oxidative fermentation, is commonly used in sauerkraut, yogurt, buttermilk, and sourdough.

Another old-world fermentation method is the production of methane from biomass, a multi-step process accomplished by a consortium of bacteria, which is an important part of the cyclical nature of carbon on our planet. These processes, now generally referred to as anaerobic digestion, are well known in ruminant animals, as well as in stagnant wet biomass. The methane from these processes has only been captured at the industrial scale for use as a fuel since the 1970s.

Additional early uses of biomass involved its structural components. The fibrous matrix (wood) was first used in constructing shelter. Later, the fibrous component was separated for paper products. As a result, two major industries, the wood products industry and the pulp and paper industry, were developed at sites where biomass was available. Biomass also comprised materials used for clothing. Cotton fibers, consisting of mainly cellulose, and flax fiber are good examples.

At the beginning of the 20th century, cellulose recovered from biomass was processed into chemical products. Cellulose nitrate was an early synthetic polymer used for "celluloid" molded plastic items and photographic film. The nitrate film was later displaced by cellulose acetate film, a less flammable and more flexible polymer. Cellulose nitrate lacquers retained their market, although acetate lacquers were also developed. Cellulose acetate fiber, called Celanese, grew to one-third of the synthetic market in the U.S. by 1940. Injection molded

cellulose acetate articles became a significant component of the young automobile industry, with 20 million pounds produced in 1939. Today, cellulose-based films and fibers have largely been supplanted by petroleum-based polymers, which are more easily manipulated to produce properties of interest, such as strength, stretch recovery, or permeability.

Wood processing to chemicals by thermal methods (pyrolysis), another practice from antiquity, was originally the method used for methanol and acetic acid recovery, but has been replaced by petrochemical processes. One of the earliest synthetic resins, the phenol-formaldehyde polymer, Bakelite, was originally produced from phenolic wood extractives. However, petrochemical sources for the starting materials displaced the renewable sources after World War I. More chemically complex products, such as terpenes and rosin chemicals, are still recovered from wood processing but only in a few cases as a byproduct from pulp and paper production.

B. CHEMURGY

Early in the 20th century, the Chemurgy movement blossomed in response to the rise in the petrochemical industry and in support of agricultural markets. The thrust of the movement was that agricultural products and food byproducts could be used to produce the chemicals important in modern society. A renewable resource, like biomass, could be harvested and transformed into products without depleting the resource base. Important industrialists, including Henry Ford, were participants in this movement, which espoused that anything made from hydrocarbons can be made from carbohydrates.

Supply inconsistencies and processing costs eventually turned the issue in favor of the petrochemical industry. The major investments for chemical process development based on hydrocarbons were more systematically coordinated within the more tightly held petrochemical industry, while the agricultural interests were too diffuse (both geographically and in terms of ownership) to marshal much of an effort. Furthermore, the chemical properties of petroleum, essentially volatile hydrocarbon liquids, allowed it to be more readily processed to chemical products. The large scale of petroleum refining operations, developed to support fuel markets, made for more efficient processing systems for chemical production as well.

III. THE “BIOREFINERY” CONCEPT

The vision of a new Chemurgy-based economy began evolving in the 1980s. The biorefinery vision foresees a processing factory that separates the biomass into component streams and then transforms the component streams into an array of products using appropriate catalytic or biochemical processes, all performed at a scale sufficient to take advantage of processing efficiencies and resulting improved process economics. In essence, this concept is the modern petroleum refinery modified to accept and process a different feedstock and make different products using some of the same unit operations along with some new unit operations. The goal is to manufacture a product slate, based on the best use of the feedstock components, which represents higher-value products with no waste. Overall process economics are improved by production of higher value products that can compete with petrochemicals. Some biomass processing plants already incorporate this concept to various degrees.

A. WOOD PULP MILL

The modern wood pulp mill represents the optimized, fully integrated processing of wood chips to products. The main process of pulping the wood allows the separation of the cellulosic fiber from the balance of the wood structure. The cellulose has numerous uses, ranging from various paper and cardboard types to chemical pulp that is further processed to cellulose-based chemicals. The lignin and hemicellulose portion of the wood are mainly converted to electrical power and steam in the recovery boiler. In some cases, the lignin is recovered as precipitated sulfonate salts, which are sold based on surfactant properties. In other cases, some lignin product is processed to vanillin favoring. The terpene chemicals can be recovered, a practice limited primarily to softwood processing plants wherein the terpene fraction is larger.

B. CORN WET MILL

In the corn wet mill, several treatment and separation processes are used to produce a range of food and chemical products. Initial treatment of the dry corn kernel in warm water with sulfur dioxide results in a softened and protein-stripped kernel and a protein-rich liquor called corn steep liquor. The corn is then milled and the germ separated. The germ is pressed and washed with solvent to recover the corn oil. Further milling and filtering separates the cornstarch from the corn fiber (essentially the seed coat). The starch is the major product and can be refined to a number of grades of starch product. It can also be hydrolyzed to glucose. The glucose, in turn, has various uses, including isomerization to fructose for high-fructose corn syrup; hydrogenation to sorbitol; or fermentation (using some of the steep liquor for nutrients) to a number of products, such as ethanol, lactic acid, or citric acid. The balance of the corn steep liquor is mixed with the corn fiber and sold as animal feed.

C. CHEESE MANUFACTURING PLANT

Cheese manufacturing has evolved in recent years into a more efficient and self-contained processing operation, where recovering the whey byproduct (as dried solids) is now the industry standard instead of disposing it, the practice for many centuries. The whey is a mostly water solution of proteins, minerals, and lactose from the milk following coagulation and separation of the cheese. To make the whey more valuable, ultrafiltration technology is now used in some plants to separate the protein from the whey for recovery as a nutritional supplement. Further processing of the ultrafiltration permeate is also used in a few plants to recover the lactose for use as a food ingredient. Methods for recovering the mineral components will be the next stage in the development process.

IV. BIOMASS-DERIVED CHEMICAL PRODUCTS

For production of chemicals from biomass, there are several processing method categories, which are used based on the product desired: fermentation of sugars to alcohol or acid products; chemical processing of carbohydrates by hydrolysis, hydrogenation, or oxidation; pyrolysis of biomass to structural fragment chemicals; or gasification by partial oxidation or steam reforming to a synthesis gas for final product formation. Various combinations of these processing steps

could be integrated in the biorefinery concept. Table II illustrates the wide range of biomass-derived chemicals. These products include the older, well-known fermentation products, as well as new products whose production methods are just being developed. Development of new processing technology is another key factor to making these products competitive in the marketplace.

Table II. Chemicals Derived From Biomass

Chemical	Derivative Chemicals	Use
<i>Fermentation Products</i>		
Ethanol		fuel
Lactic Acid	poly lactic acid	plastics
Acetone/Butanol/Ethanol		solvents
Citric Acid		food ingredient
<i>Carbohydrate Chemical Derivatives</i>		
Hydrolysate Sugars	fermentation feedstocks	fermentation products
Furfural, Hydroxymethylfurfural	furans, adiponitrile	solvents, binders
Levulinic Acid	methyltetrahydrofuran, δ -aminoLA, succinic acid	solvents, plastics, herbicide/pesticide
Polyols	glycols, glycerol	plastics, formulations
Gluconic/Glucaric Acids		plastics
<i>Pyrolysis Products</i>		
Chemical Fractions	phenolics, cyclic ketones	resins, solvents
Levogluconan, Levogluconenone		polymers
Aromatic hydrocarbons	benzene, toluene, xylenes	fuel, solvents
<i>Gasification Products</i>		
Synthesis Gas	methanol, ammonia	liquid fuels, fertilizer
Tar Chemicals		fuels
<i>Developmental Fermentations</i>		
2,3-Butanediol/Ethanol		solvents
Propionic Acid		food preservative
Glycerol, 1,3-Propanediol		C3 plastics, formulations
3-Dehydroshikimic Acid	vanillin, catechol, adipic acid	flavors, plastics
<i>Catalytic/Bioprocessing</i>		
Succinic Acid	butanediol, tetrahydrofuran	resins, solvents
Itaconic Acid	methyl-BDO and THF	resins, solvents
Glutamate, Lysine	pentanediol, pentadamine	C5 plastics
<i>Plant-Derived</i>		
Oleochemicals	methyl-esters, epoxides	fuel, solvents, binders
Polyhydroxyalkanoates		medical devices

A. MODERN FERMENTATION PRODUCTS

Fermentation products include ethanol, lactic acid, acetone/butanol/ethanol, and citric acid. Ethanol and lactic acid are produced on a scale sufficient to have an impact on energy markets. Ethanol is primarily used as a fuel, although it has numerous potential derivative products as described below. Lactic acid is new as an industrial chemical product, as the first lactate derivative product, poly lactic acid, came on stream in 2002.

1. Ethanol

In 1999, ethanol was produced at 55 plants around the U.S. at a scale of 1.8 billion gallons per year. The feedstock for the fermentation ranges from corn starch-derived glucose, wheat gluten production byproduct starches, and cheese whey lactose to food processing wastes and, until recently, wood pulping byproducts. Although some of this ethanol is potable and goes into the food market, the vast majority is destined for the fuel market for blending with gasoline (as described elsewhere in this Encyclopedia). However, other possible chemical products derived from ethanol include acetaldehyde, acetic acid, butadiene, ethylene, and various esters, some of which were used in the past and may again become economically viable.

2. Lactic Acid

Lactic acid, as currently utilized, is an intermediate volume specialty chemical, used in the food industry for producing emulsifying agents and as a non-volatile, odor-free acidulant, with a world production of about 100 million pounds per year in 1995. Its production by carbohydrate fermentation involves any of several *lactobacillus* strains. The fermentation can produce a desired stereoisomer, unlike the chemical process practiced in some parts of the world. Typical fermentation produces a 10% concentration lactic acid broth, which is kept neutral by addition of calcium carbonate throughout the 4- to 6-day fermentation. Using the fermentation-derived lactic acid for chemical products requires complicated separation and purification, including the reacidification of the calcium lactate salt and resulting disposal of a calcium sulfate sludge byproduct. An electrodialysis membrane separation method, in the development stage, may result in an economical process. The lactic acid can be recovered as lactide by removing the water, which results in the dimerization of the lactic acid to lactide that can then be recovered by distillation.

Poly lactic acid (PLA) is the homo-polymer of biomass-derived lactic acid, usually produced by a ring-opening polymerization reaction from its lactide form. It is the first generic fiber designated by the Federal Trade Commission in the 21st century, and the first renewable chemical product commercially produced on an industrial scale. Cargill-Dow, LLC, who is producing PLA, opened its plant rated at 300 million pounds per year capacity in April 2002. Other chemical products that can be derived from lactic acid include lactate esters, propylene glycol, and acrylates. The esters are described as nonvolatile, nontoxic, and biodegradable with important solvent properties. Propylene glycol can be produced by a simple catalytic hydrogenation of the lactic acid molecule. Propylene glycol is a commodity chemical with a billion pound per year market and can be used in polymer synthesis and as a low-toxicity antifreeze and deicer. Dehydration of lactate to acrylate appears to be a straightforward chemical process, yet a high yield process is still to be commercialized.

3. Acetone/Butanol/Ethanol

Acetone/butanol/ethanol (ABE) fermentation was widely practiced in the early part of the 20th century before being displaced by petrochemical operations. The two-step bacterial fermentation is carried out by various species of the *Clostridium* genus. The solvent product ratio is typically 3:6:1, but, due to its toxicity, the butanol product is the limiting component. The yield is only 37%, and final concentrations are approximately 2%. The high energy cost for recovery by distillation of the chemical products from such a dilute broth is a major economic drawback. Alternative recovery methods, such as selective membranes, have not yet been demonstrated.

4. Citric Acid

Over 1 billion pounds per year of citric acid are produced worldwide. The process is a fungal fermentation with *Aspergillus niger* species using a submerged fermentation. About one-third of the production is in the U.S., and most of it goes into beverage products. Chemical uses will depend on the development of appropriate processes to produce derivative products.

B. CHEMICAL PROCESSING OF CARBOHYDRATES

1. Hydrolysate Sugars

Monosaccharide sugars can be derived from biomass and used as final products or further processed by catalytic or biological processes to final value-added products. Disaccharides, such as sucrose, can be recovered from plants and used as common table sugar or “inverted” (hydrolyzed) to a mixture of glucose and fructose. Starch components in biomass can readily be hydrolyzed to glucose by chemical processes (typically acid-catalyzed) or more conventionally by enzymatic processes. Inulin is a similar polysaccharide recovered from sugar beets that could serve as a source of fructose. More complex carbohydrates such as cellulose or even hemicellulose can also be hydrolyzed to monosaccharides. Acid-catalyzed hydrolysis has been studied extensively and is used in some countries to produce glucose from wood. The processing parameters of acidity, temperature, and residence time can be controlled to fractionate biomass polysaccharides into component streams of primarily 5- and 6-carbon sugars based on the relative stabilities of the polysaccharides. However, fractionation to levels of selectivity sufficient for commercialization has not yet been accomplished.

The development of economical enzymatic processes for glucose production from cellulose could provide a tremendous boost for chemicals production from biomass. The even more complex hydrolysis of hemicellulose for monosaccharide production provides a potentially larger opportunity, because there are fewer alternative uses for hemicellulose than cellulose.

2. Furfural, Hydroxymethylfurfural, and Derived Products

More severe hydrolysis of carbohydrates can lead to dehydrated-sugar products such as the furfural from 5-carbon sugar and hydroxymethylfurfural from 6-carbon sugar. In fact, the careful control of the hydrolysis to selectively produce sugars without further conversion to furfurals is an important consideration in the hydrolysis of biomass when sugars are the desired products. However, furfural products are economically valuable in their own right. The practice of processing the hemicellulose 5-carbon sugars in oat hulls to furfural has continued despite economic pressure from petrochemical growth, and is still an important process with an annual domestic production at about 100 million pounds. Furfural can be further transformed into a

number of products, including furfural alcohol and furan. Even adiponitrile was produced from furfural for nylon from 1946 to 1961.

3. Levulinic Acid and Derived Products

Levulinic acid, 4-oxo-pentanoic acid, results from subsequent hydrolysis of hydroxymethylfurfural. It is relatively stable toward further chemical reaction at hydrolysis conditions. Processes have been developed to produce it from wood, cellulose, starch, or glucose.

Levulinic acid is potentially a useful chemical compound based on its multi-functionality and its many potential derivatives. Over the last half of the 20th century its potential for derivative chemical products was reviewed numerous times in the chemical literature. Some examples of the useful products described include: levulinate esters, with useful solvent properties; δ -aminolevulinic acid, identified as having useful properties as a herbicide and for potentially controlling cancer; hydrogenation of levulinic acid, which can produce γ -valerolactone, a potentially useful polyester monomer (as hydroxyvaleric acid); 1,4-pentanediol, also of value in polyester production; methyltetrahydrofuran, a valuable solvent or a gasoline blending component; and diphenolic acid, with potential for use in polycarbonate production.

4. Hydrogenation to Polyols

Sugars can readily be hydrogenated to sugar alcohols at relatively mild conditions using a metal catalyst. Some examples of this type of processing include: sorbitol produced from glucose; xylitol produced from xylose; lactitol produced from lactose; and maltitol produced from maltose. All of these sugar alcohols have current markets as food chemicals. New chemical markets are now developing; for example, sorbitol has been demonstrated in environmentally friendly deicing solutions.

In addition, the sugar alcohols can be further processed to other useful chemical products. Isosorbide is a doubly-dehydrated product from sorbitol produced over an acid catalyst. Isosorbide has uses in polymer blending, for example, to improve the rigidity of polyethylene terephthalate in food containers, like soda-pop bottles.

Hydrogenation of the sugar alcohols at more severe conditions can be applied to produce lower-molecular-weight polyols. By this catalytic hydrogenolysis, 5- or 6-carbon sugar alcohols have been used to produce primarily a three-product slate consisting of propylene glycol, ethylene glycol, and glycerol. While other polyols and alcohols are also produced in lower quantities, these three are the main products from hydrogenolysis of any of the epimers of sorbitol or xylitol. Product separations and purifications result in major energy requirements and costs. Consequently, controlling the selectivity within this product slate is a key issue in commercializing the technology. Selectivity can be affected by processing conditions as well as catalyst formulations.

5. Oxidation to Gluconic/Gluconic Acid

Glucose oxidation can be used to produce 6-carbon hydroxyacids, either the monoacid, gluconic, or the diacid, gluconic. The structures of these chemicals suggest opportunities for polyester and polyamide formation, particularly polyhydroxypolyamides, i.e., hydroxylated nylon. The oxidation is reported to be performed economically with nitric acid as the catalyst. Specificity to

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the desired product remains to be overcome before these chemicals can be produced commercially.

C. POTENTIAL PYROLYSIS PRODUCTS

Pyrolysis of wood for chemicals and fuels production has been practiced for centuries; in fact, it was likely the first chemical production process known to humans. Early products of charcoal and tar were used not only as fuels but also for embalming, filling wood joints, among other uses. Today, pyrolysis is still important in some societies, but has largely been displaced by petrochemical production in the developed countries. At the beginning of the 20th century, important chemical products were methanol, acetic acid, and acetone. Millions of pounds of these products were produced by wood pyrolysis until about 1970, when economic pressure caused by competition with petroleum-derived products became too great. Based on new developments in “flash” pyrolysis beginning in the 1980s, there are new movements into the market with wood pyrolysis chemicals. However, these products are specialty chemicals and not yet produced on a commodity scale.

1. Chemical Fractions

Most new development work in pyrolysis involves separating the bulk fractions of chemicals in the pyrolysis oil. Heavy phenolic tar can be separated simply by adding water. A conventional organic chemical analytical separation uses base extraction for acid functional types, including phenolics. Combining the water addition step and the base extraction with a further solvent separation can result in a stream of phenolics and neutrals in excess of 30% of the pyrolysis oil. This stream has been tested as a substitute for phenol into phenol-formaldehyde resins commonly used in restructured wood-based construction materials, such as plywood and particle board. This application allows for the use of the diverse mixture of phenolic compounds produced in the pyrolysis process, which typically includes a range of phenols, alkyl-substituted with 1- to 3-carbon side chains, and a mix of methoxyphenols (mono-methoxy from softwoods and a mix of mono- and di-methoxy phenols from hardwood) with similar alkyl substitution. In addition, there are more complex phenolics with various oxygenated side chains, suggesting the presumed source -- lignin in the wood.

The lower-molecular-weight non-phenolics remain a significant but smaller fraction of pyrolysis oil as produced in “flash” processes. Methanol and acetic acid recovery has potential opportunities. Other opportunities include hydroxyacetaldehyde, formic acid, hydroxyacetone, and numerous small ketones and cyclic ketones, which may have value in fragrances and flavorings.

2. Levoglucosan and Levoglucosenone

Cellulose pyrolysis can result in relatively high yields of levoglucosan or its subsequent derivative levoglucosenone. Both are dehydration products from glucose. The levoglucosan is the 1,6-anhydro product, and the levoglucosenone results from removal of two of the three remaining hydroxyl groups of levoglucosan with the formation of a conjugated olefin double bond and a carbonyl group. Levoglucosenone’s chiral nature and its unsaturated character suggest uses for this compound in pharmaceuticals as well as in polymer formation.

3. Aromatic Hydrocarbon Compounds - BTX

The large fraction of phenolic compounds in pyrolysis oil suggests the formation of aromatics for chemical or fuel use. Catalytic hydrogenation (in this case, hydrodeoxygenation) can be used for removing the hydroxyl group from the phenolic compounds to produce the respective phenyl compound. For example, hydrogenation of phenol or methoxyphenol (guaiacol) would give benzene, and methyl-guaiacol would give toluene. This chemistry was studied in the 1980s when aromatics were being added to gasoline to improve octane number. With increased restriction on aromatics in gasoline to meet emission guidelines, this process concept was shelved. Production of such hydrocarbons (and other saturated cyclic hydrocarbons) remains an option for chemical production from wood pyrolysis; however, the economics are a drawback, with the extensive amount of hydrogenation required to convert the oxygenate to a hydrocarbon.

D. POTENTIAL GASIFICATION PRODUCTS

Whereas the pyrolysis process results in a product that retains much of the chemical functional character of the biomass feedstock, gasification operates at more severe process conditions and results in products of relatively a simple chemical structure but with wide applications. Gasification usually entails high-temperature partial oxidation or steam reforming of the biomass feedstock with typical products of hydrogen, carbon monoxide and dioxide, and light hydrocarbons. Other gasification processes using catalysis or bioconversion methods can also result in a primarily methane and carbon dioxide product gas.

1. Synthesis Gas to Produce Chemicals

Synthesis gas produced from biomass can be used for chemical production in much the same way as synthesis gas from steam reforming of natural gas or naphtha. Certain process configurations can be used with proper optimization or catalysis to control the all-important ratio of hydrogen to carbon monoxide in the synthesis gas. The synthesis gas can then be used in catalyzed reactions to produce methanol or hydrocarbons, or even ammonia. Methanol can subsequently be converted by further catalytic steps to formaldehyde, acetic acid, or even gasoline.

2. Tar Chemicals

Byproducts formed in incomplete gasification include an array of organics ranging from the pyrolysis chemicals to further reacted products that include aromatics and, particularly, polycyclic aromatics, if sufficient severity of time at high temperature is applied. As a function of temperature and time at temperature, the composition of the tar can vary from a highly oxygenated pyrolysis oil produced at lower temperature and short residence time to a nearly deoxygenated polycyclic aromatic hydrocarbon produced at high temperature. These high-temperature tar components, including 4- and 5-aromatic ring structures, put them into the range where mutagenic activity can be significant.

E. DEVELOPMENTAL FERMENTATIONS

New fermentation processes for additional biomass-derived chemical products are various developmental stages. These new processes range from improvements to known fermentations to new chemical products produced in genetically engineered organisms.

1. Acetic Acid

Acetic acid is a major organic chemical commodity product with an annual domestic demand in excess of 6 billion pounds. The acetic acid currently available for chemical uses is petrochemically derived. Acetic acid fermentation, known from antiquity to form vinegar, is an *Acetobacter* partial oxidation of ethanol. More recently developed is the homo-fermentative conversion of glucose to acetic acid by “acetogenic” *Clostridium* bacteria. In some cases, 3 moles of acetate can be produced from each mole of 6-carbon sugar feedstock, and concentrations of acetate of up to 1.5% can be accumulated. This type of fermentation effectively increases the theoretical yield of acetic acid from glucose by 50% and provides a more reasonable pathway from renewable resources.

2. Propionic Acid

All chemical production of propionic acid, best known as a food preservative, is currently derived from petroleum as a coproduct or byproduct of several processes. However, propionic acid can readily be fermented with propionibacterium. Domestic production is at about 220 million pounds per year and growing only by 1% to 2% annually. A small but growing market is the production of esters for use as environmentally benign solvents.

3. Extremophilic Lactic Acid

As an economical production process, lactic acid fermentation from glucose has led the way into the marketplace for chemicals production. While the lactic acid process used for PLA production is based on conventional fermentation, the recovery of the lactide product for polymerization eliminates the neutralization and reacidification steps typically required. Process improvement efforts are focusing on the development of new organisms that can function at acidic conditions and produce higher concentrations of lactic acid. These organisms, termed extremophiles, are expected to operate at a pH below 2 in a manner similar to citric acid fermentations. Other work to produce higher-temperature-tolerant organisms may also result in reduced production costs.

4. 2,3-Butanediol/Ethanol

For this fermentation, a variety of different bacterial strains can be used. An equimolar product mix is produced under aerobic conditions, while limited aeration will increase the production of the 2,3-butanediol to the level of exclusivity. Either optically active 2,3-butanediol or a racemic mixture can be produced, depending on the bacterial strain. Similarly, the final product concentration, ranging from 2-3% up to 6-8%, depends on bacterial strain. Recovering the high-boiling diol by distillation is still problematic.

5. Succinic Acid

Succinate production from glucose and other carbohydrates has been well-characterized for numerous bacterial organisms, including several *succinogenes* and the *anaerobiospirillum succiniproducens*. The biological pathways for these organisms are similar and usually result in significant acetate production as well. The pathway also includes a carbon dioxide insertion step such that potential theoretical yield is greater than 100% based on glucose feedstock. Mutated *E. coli* have also been developed for succinic acid production, with yields as high as 90% shown on the pilot scale and a final succinic acid concentration in the 4% to 5% range. As with lactic acid

production, maintaining the pH of the fermentor at about neutral is vital. The resulting disposal of mineral byproducts from neutralization and reacidification is problematic. New advances in membrane separation methods or acid-tolerant fermentation organisms are important elements of commercially developing succinic acid production.

6. Itaconic Acid

Itaconic acid is succinic acid with a methylene group substituted onto the carbon chain. It is typically produced in a fungal fermentation at relatively small scale and high cost (\$1.2 to \$2/lb). Feasibly, the economics of this fermentation could be improved in a manner similar to that seen in the past for citric acid fermentation. As a result, itaconic acid could become available for use directly in polymer applications, as well as for further processing to value-added chemical products.

7. Glycerol and 1,3-PDO

Bacterial fermentation of glycerol to 1,3-propanediol (PDO) has been studied as a potential renewable chemical production process. The glycerol feedstock would be generated as byproduct from vegetable oil conversion to diesel fuel (biodiesel). The anaerobic conversion of glycerol to PDO has been identified in several bacterial strains, with *Clostridium butyricum* most often cited. The theoretical molar yield is 72%, and final product concentration is kinetically limited to about 6% to 7%. The PDO product is a relatively new polyester source, only recently becoming economically available from petroleum sources. Its improved properties as a fiber include both stain resistance and easier dye application.

8. 3-Dehydroshikimic acid (DHS)

This interesting building block has been identified as a potential renewable resource. It is a hydroaromatic intermediate in the aromatic amino acid biosynthetic pathway. Its formation in mutated *E. coli* and its recovery in significant yields have been reported. It can be produced from 6-carbon sugars with theoretical yield of 43%, while a 71% yield is theoretical from 5-carbon sugars based on a different metabolic pathway. Further processing of DHS can lead to protocatechuic acid, vanillin, catechol, gallic acid, and adipic acid.

F. CATALYTIC/BIOPROCESSING COMBINATIONS

Combining bioprocessing systems with catalytic processing systems provides some important opportunities for biomass conversion to chemicals. While fermentation of biomass feedstocks to useful chemicals can be a direct processing step, in many cases the fermentation product can, in turn, be transformed into a range of value-added chemical products. By this philosophy, the fermentation product acts as a platform chemical from which numerous final products can be derived. Some of these combined bioprocessing platform chemicals and catalytically derived families of value-added chemicals are described below.

1. Succinic Acid Derivatives

Two branches of the succinic acid family tree have been described. The first, involving hydrogenation, is similar to hydrogenation of maleic anhydride performed in the petrochemical industry based on butane oxidation. The hydrogenation products from succinic acid include γ -butyrolactone, 1,4-butanediol (BDO), and tetrahydrofuran (THF). BDO and THF are currently

750-million-pound chemical products. The lactone and THF have solvent markets, while BDO is an important polyester resin monomer (polybutylene terephthalate). THF is also used for Spandex fiber production.

The second pathway for succinic acid chemical production is through the succinamide to form pyrrolidones. N-methylpyrrolidone is an important low-toxicity, environmentally benign solvent with a growing annual market of over 100 million pounds, displacing chlorinated hydrocarbon solvents. 2-pyrrolidone can form the basis for several polymers, including polyvinyl pyrrolidone.

2. Itaconic Acid Derivatives

Itaconic acid's similarity of structure to succinic acid suggests that it could be used to produce similar families of chemical products. Typically, the products would be methylated versions of the succinic-derived products, such as 2-methyl-1,4-butanediol; 3-methyltetrahydrofuran; or 3-methyl-N-methylpyrrolidone. Therefore, the final products would include methylated polyesters or methylated Spandex.

3. Glutamic Acid and Lysine

Glutamic acid and lysine are already major chemical products, with the glutamate sold as the sodium salt, monosodium glutamate (MSG), and lysine used as an important animal feed supplement. Both compounds are produced industrially by fermentation.

Glutamate is produced as the L-glutamic acid at 680 million pounds per year, with 85% of the production in Asia. In the first half of the 20th century, glutamate was produced by hydrolysis of protein, primarily wheat gluten. The current fermentation process, using molasses or other cheap glucose source, replaced protein hydrolysis processing by 1965. Glutamate's current cost of over \$1.4/lb is too high for use as a platform chemical and its use for chemical production is dependent on improved fermentation, recovery method modification, and integration of catalytic processing with the existing fermentation process.

Worldwide lysine production is at a lower level than glutamate, only about one-third. As a result, its cost is about double that of glutamate. Consequently, chemical production based on glutamate rather than lysine-based production appears to be more likely.

Glutamate and lysine are interesting as renewable chemical feedstocks, as each provides both multi-functionality and a 5-carbon backbone. The 5-carbon-based polymers are not widely used and are less well-known or understood, since no easy route to 5-carbon petroleum products exists. Processing steps can be envisioned for direct conversion of glutamate either to a 5-carbon diacid by deamination (or thereafter to 1,5-pentanediol) for polyester production or to a 5-carbon terminal amine/acid for nylon production. Lysine could be decarboxylated to produce a 5-carbon diamine or could be deaminated to the amine/acid (the same as from glutamate) for nylon production.

G. PLANT-DERIVED CHEMICALS

One strategy for the use of biomass for chemicals production is the recovery of chemical products produced directly by plants. This strategy can involve either the recovery from existing plants, such as the oils from certain seed crops, or from genetically modified plants in which the chemical is produced specifically for harvesting.

1. Oleochemicals

The oil recovered from certain seed crops has been an important food product for many centuries. The growth of scale of the processing industry in the case of corn and soybeans has reduced the cost of the oil to the point that it can be considered for use in commodity chemical products. The use of vegetable oil for fuel as the trans-esterified methyl esters of the fatty acids derived from the triglycerides, known as biodiesel, has made some market inroads but primarily to meet alternative fuel use requirements and not based on demand. An important market breakthrough for renewable resources was the use of soybean oils in printing inks, instituted in the 1990s, which has been growing steadily. New uses include toners for photocopy machines and in adhesive formulations. Other uses, such as plasticizers or binders based on epoxide formation from the unsaturated fatty acids, have also been investigated.

2. Polyhydroxyalkanoates

Polyhydroxyalkanoate (PHA) production has been demonstrated by both fermentative and plant growth methods. PHA is a biodegradable polymer with applications in the biomedical field. Originally, PHA was limited to polyhydroxybutyrate (PHB), but it was found to be too brittle. A copolymer (PHBV) of 75% hydroxybutyrate and 25% hydroxyvalerate is now a commercial product with applications in medical devices. However, the fermentative process has potentially has some significant drawbacks that, when considered on a life-cycle basis, could result in a poorer performance for polyhydroxyalkanoate production from a renewable perspective than petroleum-derived polystyrene. To address these drawbacks, which include high energy requirements for cell wall rupture and product recovery, plant-based production of PHA has been investigated using genetic modification to engineer the PHB production pathway into *Arabidopsis* as the host plant. Alternatively, the PHBV might be produced by other organisms that can use multiple sugar forms from a less-refined biomass feedstock than corn-derived glucose.

V. THE FUTURE BIOREFINERY

The future biorefinery (Fig. 1) is conceptualized as an optimized collection of the various process options described above. In addition to the several chemical processing steps to produce value-added chemicals, it would likely incorporate components from existing biorefinery-type operations, such as wood pulp mill, wet corn mill, and cheese manufacturing processes.

Carbohydrate separation and recovery would likely involve both the 5-carbon and 6-carbon compounds. These compounds would respond to separations by selective hydrolysis, as the 5-carbon and 6-carbon compounds have different activities in either chemical or enzymatic hydrolyses. Any oil or protein components liberated through this processing would be considered as potential high-value chemicals. The lignin components, the least developed of the biomass fractions, is often viewed as a fuel to drive the processing systems, but also remains a potential source of aromatic chemical products. Mineral recovery is most likely to be important to maintain agricultural productivity with the return of the minerals to the croplands as fertilizer.

In order to reach a true biorefinery status, each biomass component would be used in the appropriate process to yield the highest-value product. Therefore, a combination of processing steps, tailored to fit the particular operation, would be used to produce a slate of chemical

products. The slate of products would be developed in response to the market drivers to optimize feedstock utilization and overall plant income. In this manner, the return on investment for converting low-cost feedstock to high-value chemical products can be maximized.

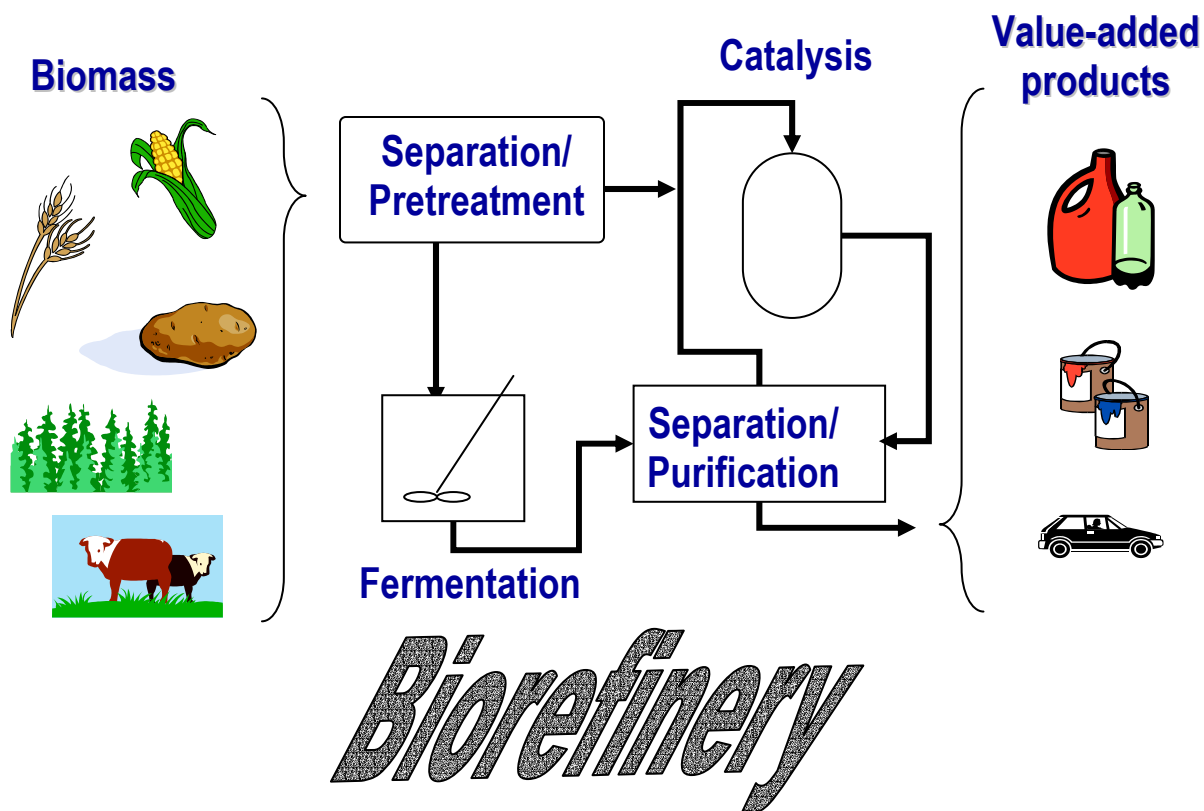


Figure 1. Biorefinery concept for production of value-added chemicals from biomass.

The future biorefinery will likely have a major impact on society as fossil-derived resources become scarce and more expensive. Indeed, use of biomass provides the only option for maintaining the supply of new carbon-based chemical products to meet society's demands. The biorefinery can provide a positive environmental impact by deriving its carbon source (via plants) through reducing atmospheric levels of carbon dioxide, an important greenhouse gas. With appropriate attention to the fates of biomass-derived nitrogen and mineral components in the biorefinery processes, a life-cycle balance may be achieved for these nutrient materials, if their recovery efficiencies can be maintained at high levels.

BIBLIOGRAPHY

- Arntzen, C.J., Dale, B.E. et al. (2000). *Biobased Industrial Products*. National Academy Press, Washington, D.C.
- Bozell, J.J. (ed.) (2001). *Chemicals and Materials from Renewable Resources: ACS Symposium Series #784*. American Chemical Society, Washington, D.C.
- Bozell, J. J., and Landucci, R. (eds.) (1993). *Alternative Feedstocks Program, Technical and Economic Assessment: Thermal/Chemical and Bioprocessing Components*. National Renewable Energy Laboratory, Golden, CO.
- Donaldson, T.L., and Culberson, O.L. (1983). *Chemicals from Biomass: An Assessment of the Potential for Production of Chemical Feedstocks from Renewable Resources*. ORNL/TM-8432, Oak Ridge National Laboratory, Oak Ridge, TN.
- Executive Steering Committee, Renewables Vision 2020. (1999). *The Technology Roadmap for Plant/Crop-Based Renewable Resources 2020*. DOE/GO-10099-706, U.S. Department of Energy, Washington, DC.
- Fuller, G., McKeon, T. A., and Bills, D. D. (eds.) (1996). *Agricultural Materials as Renewable Resources – Nonfood and Industrial Applications: ACS Symposium Series #647*. American Chemical Society, Washington, D.C.
- Goldstein, I. S. (ed.) (1981). *Organic Chemicals from Biomass*. CRC Press, Boca Raton, FL.
- Morris, D., and Ahmed, I. (1992). *The Carbohydrate Economy: Making Chemicals and Industrial Materials from Plant Matter*. Institute for Local Self-Reliance, Washington, D.C.
- Rowell, R. M., Schultz, T. P. and Narayan, R. (eds.) (1992). *Emerging Technologies for Materials and Chemicals from Biomass: ACS Symposium Series #476*. American Chemical Society, Washington, D.C.
- Saha, B. C., and Woodward, J. (eds.) (1997). *Fuels and Chemicals from Biomass: ACS Symposium Series #666*. American Chemical Society, Washington, D.C.
- Scholz, C., and Gross, R. A. (eds.) (2000). *Polymers from Renewable Resources – Biopolyesters and Biocatalysis: ACS Symposium Series #764*. American Chemical Society, Washington, D.C.
- St-Pierre, L. E., and Brown, G. R. (eds.) (1980). *Future Sources of Organic Raw Materials: CHEMRAWN I*. Pergamon Press, Oxford, U.K.