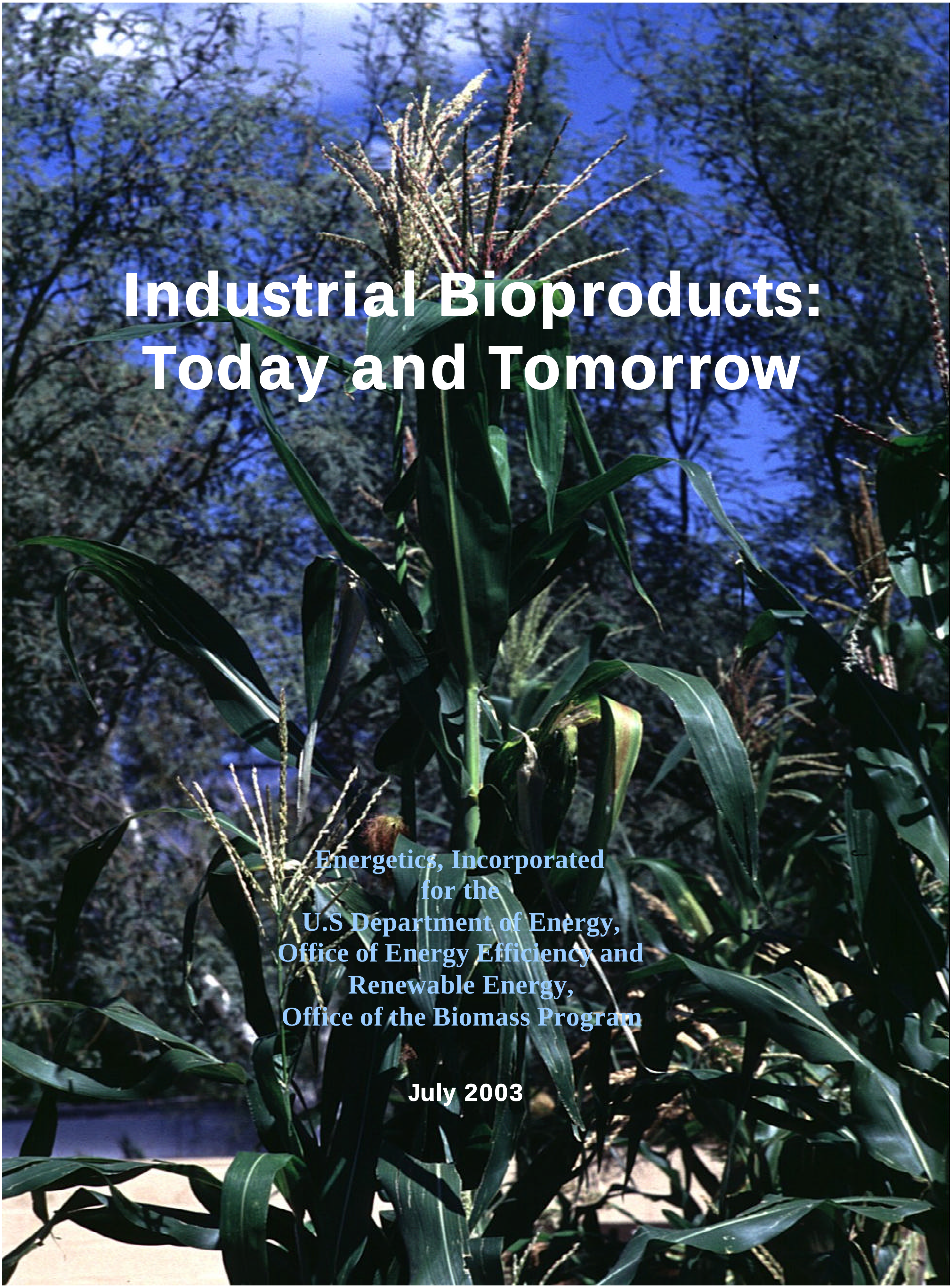

Industrial Bioproducts: Today and Tomorrow

Energetics, Incorporated
for the
U.S Department of Energy,
Office of Energy Efficiency and
Renewable Energy,
Office of the Biomass Program

July 2003

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Preface

Today the U.S. economy is dominated by technologies that rely on fossil energy (petroleum, coal, natural gas) to produce fuels, power, chemicals and materials. Biomass presents a promising renewable energy opportunity that could provide an alternative to the use of fossil resources. A bioindustry could harness the energy and molecular building blocks of biomass (crops, trees, grasses, crop residues, forest residues, animal wastes, and municipal solid waste) to create products that are now manufactured from petroleum. New industrial biorefineries could produce biobased products, fuels and power for our economy making us far less dependent on fossil fuels.

As a domestic energy source, biomass is naturally abundant. In the continental United States, about 500 to 600 million tons of plant matter can be grown and harvested in addition to our food and feed needs. These abundant biomass resources can be used to significantly enhance our nation's energy independence and security over the long term by reducing the use of imported oil and increasing the reliability of energy supplies. Today, the United States imports over 7 barrels of oil for every 5 barrels produced domestically. This heavy dependence on imported oil negatively affects the U.S. trade balance and exposes our economy to potential disruptions in supply. Volatilities in the price and availability of fossil energy also create economic and social uncertainties for businesses and individuals. A bioindustry could help meet demand for energy and products, and leverage our limited fossil energy resources. A bioindustry could provide other benefits such as productive use of agricultural and forestry wastes, lower emissions of greenhouse gases and pollutants, and growth in rural economies.

At the U.S. Department of Energy (DOE), Office of Energy Efficiency and Renewable Energy (EERE), fostering a new bioindustry is a high priority. EERE recognizes the significant potential of biomass and the opportunities it represents to enhance our energy security. In view of this potential, EERE has established the Office of the Biomass Program (OBP) to promote the use of this valuable energy resource. The activities conducted by OBP will foster development of the technologies needed to drive the growth of a new bioindustry.

Industrial bioproducts – chemicals and materials produced from biomass – play a key role in the OBP strategy for fostering a new bioindustry. There is a tremendous potential to supplement and supplant the petroleum resources used today to manufacture billions of pounds of important chemical products. In the current marketplace, the manufacture of these industrial chemicals and materials consumes about 6.5 quadrillion Btu (quads) of petroleum equivalents, or about 1 billion barrels of oil every year. The available biomass resources represent as much as 6-10 quads of feedstock energy – or enough energy to manufacture more than 300 billion pounds of organic chemicals.

Industries are already beginning to take advantage of the opportunities and become a part of the new bioindustry. This report examines the current state of industrial bioproducts, emerging products and technology, and the potential opportunities for growth in the next two decades.

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1.0 Overview of Industrial Bioproducts

1.1 The Nature of Industrial Bioproducts

Bioproducts are industrial and consumer goods manufactured wholly or in part from renewable biomass (plant-based resources). Today's industrial bioproducts are amazingly diverse, ranging from solvents and paints to pharmaceuticals, soaps, cosmetics and building materials (see Table 1-1). Industrial bioproducts are integral to our way of life -- few sectors of the economy do not rely in some way on products made from biomass.

Table 1-1 Common Products From Biomass

Biomass Resource	Uses
Corn	Solvents, pharmaceuticals, adhesives, starch, resins, binders, polymers, cleaners, ethanol
Vegetable Oils	Surfactants in soaps and detergents, pharmaceuticals (inactive ingredients), inks, paints, resins, cosmetics, fatty acids, lubricants, biodiesel
Wood	Paper, building materials, cellulose for fibers and polymers, resins, binders, adhesives, coatings, paints, inks, fatty acids, road and roofing pitch

Corn, wood, soybeans, and plant oils are the primary resources used to create this remarkable diversity of industrial and consumer goods. In some cases, it is not readily apparent that a product is derived in part from biomass. Biomass components are often combined with other materials such as petrochemicals and minerals to manufacture the final product. Soybean oil, for example, is blended with other components to produce paints, toiletries, solvents, inks, and pharmaceuticals. Some products, such as starch adhesives, are derived entirely from biomass.

The many derivatives of corn illustrate the diversity of products that can be obtained from a single biomass resource (see Figure 1-1). Besides being an important source of food and feed, corn serves as a feedstock for ethanol and sorbitol, industrial starches and sweeteners, citric and lactic acid, and many other products. Products and derivatives for the major biomass feedstocks are given in Appendix A.

Biomass, which is comprised of carbohydrates, can be used to produce some of the products that are commonly manufactured from petroleum and natural gas, or hydrocarbons. Both resources contain the essential elements of carbon and hydrogen. In some cases, both resources have captured a portion of market share (see Table 1-2).

Table 1-2 Products from Hydrocarbons Versus Carbohydrates

Product	Total Production (million tons)	% Derived From Plants
Adhesives	5.0	40
Fatty Acids	2.5	40
Surfactants	3.5	35
Acetic Acid	2.3	17.5
Plasticizers	0.8	15
Activated Carbon	1.5	12
Detergents	12.6	11
Pigments	15.5	6
Dyes	4.5	6
Wall Paints	7.8	3.5
Inks	3.5	3.5
Plastics	30	1.8

Source: ILSR 1992

Classes of Bioproducts

The thousands of different industrial bioproducts produced today can be categorized into four major areas:

- ***Sugar and starch bioproducts*** derived through fermentation and thermochemical processes include alcohols, acids, starch, xanthum gum, and other products derived from biomass sugars. Primary feedstocks include sugarcane, sugarbeets, corn, wheat, rice, potatoes, barley, sorghum grain, and wood.

- ***Oil- and lipid- based bioproducts*** include fatty acids, oils, alkyd resins, glycerine, and a variety of vegetable oils derived from soybeans, rapeseed, or other oilseeds.

- ***Gum and wood chemicals*** include tall oil, alkyd resins, rosins, pitch, fatty acids, turpentine, and other chemicals derived from trees.

- ***Cellulose derivatives, fibers and plastics*** include products derived from cellulose, including cellulose acetate (cellophane) and triacetate, cellulose nitrate, alkali cellulose, and regenerated cellulose. The primary sources of cellulose are bleached wood pulp and cotton linters.

- ***Industrial enzymes*** are used as biocatalysts for a variety of biochemical reactions in the production of starch and sugar, alcohols, and oils. They are also used in laundry detergents, tanning of leathers and textile sizing [Uhlig 1998].

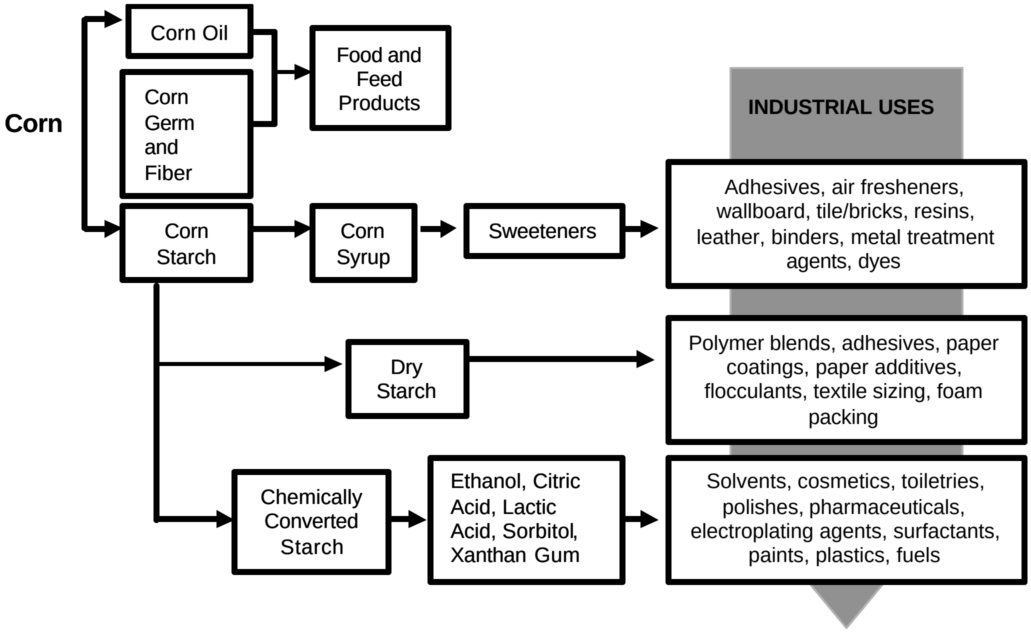


Figure 1-1 Bioproducts From Corn Grain

Scope of this Report and Data

Included in this report:

- Industrial bioproducts, i.e.,chemicals and materials produced from biomass, including those made from imported biomass.

Excluded:

- Forest products (lumber, paper, oriented strand board, and plywood), food, food ingredients, food by-products, nutraceuticals, flavor ingredients, biofuels, pharmaceuticals, and textiles.

The bioproducts industry is newly emerging as an individual entity and is not established under a single North American Industrial Classification System (NAICS) code. Companies producing biomass feedstocks and/or bioproducts fall under food processing (NAICS 311), chemicals (NAICS 325) or under multiple classifications (see Table 1-3).

The NAICS categories may include products manufactured from biomass as well as from other sources, such as petrochemicals, and products that are used for food rather than industrial purposes. This overlap makes it difficult to aggregate statistics for the bioproducts industry. Some of the statistics shown in this report are thus derived using the average percents shown in Table 1-3.

Overview of Current Production

Although data varies considerably between sources (see Table 1-4), it has been estimated that about 12 billion pounds of domestic biomass goes into industrial and consumer products every year. Differences in estimates provided by these studies result mostly from variations in the definition of what should be included as a bioproduct (e.g., industrial proteins, products that are not entirely biomass-derived), and whether to include products made from imported biomass.

Table 1-4 Comparison of Bioproducts Baselines

Study	Baseline (billion lb)
Institute for Local Self-Reliance, 1992[1]	13
National Renewable Energy Laboratory, 2001[2]	21.1
Arthur D. Little, 2001[3]	17.4
Energetics, Inc., 2001[4]	12.4

Sources: ILSR 1992, NREL 2001, ADL 2001, EI 2001

Table 1-5 illustrates the production and economic value of selected major bioproducts, based primarily on data available from the U.S. Department of Commerce. To quantify the current value of bioproducts, a profile was developed using the percents shown in Table 1-3. Within this profile, the value of bioproducts is estimated to be about $8 billion per year [DOC-ASM 1999].

Table 1-3 NAICS Characterizing the Bioproducts Industry

NAICS (SIC)	Major Products	% Industrial Bioproducts
325193 Ethyl Alcohol fermented, for industrial purposes (previously part of Industrial Organic Chemicals, NEC SIC 2869)	Non-potable ethanol for fuel and industrial purposes	3-5
325191, Gum and Wood Chemical Manufacturing (SIC 2861)	Tall oil, rosin, pine oil, turpentine, wood alcohol, hardwood and softwood distillates, tar and tar oils	100
325221 Cellulosic Manmade Fibers (SIC 2823)	Cellulose acetate, acetate fibers, cellulose fibers, rayon fibers and yard, triacetate fibers, regenerated cellulose fibers, cellulosic yarns	100
311221 Wet Corn Milling (SIC 2046)	Corn sweeteners, starch and dextrin, corn oil, corn gluten	26
311222 Soybean Oil Mills (SIC 2075)	Soybean oil, cake and meal, soybean protein isolates, and non-edible soybean oils	4-6
311223 Other Oilseed Processing (previously Vegetable Oil Mills SIC 2076 and SIC 2074 Cottonseed Oil Mills)	Cottonseed oil and linters, linseed oil, palm oil, sunflower seed oil, tung oil, vegetable oil	2-100**
325611 Soap and Other Detergents (SIC 2841)	Detergents, soap, natural glycerin, washing compounds	11
325613 Surface Active Agents (SIC 2843)	Calcium and sodium salts of oils, fats or greases, soluble oils and greases, surfactants	35

Sources: ILSR 1992, DOC-ASM 1999.
*Estimated based on known feedstocks and published production values for bioproducts.
** Many of these oils are imported, and data on end-use is only available for some products.

Table 1-5 Production of Selected Bioproducts

Products/ Intermediates	Annual Production (million lbs)	Estimated Value (million $)
Wood & Gum Chemicals *	3,268	890
Cellulose Fibers	360	760
Cellulose Derivatives **	2,140	1,400
Industrial Corn Starch and Corn Chemicals	6,500	2,200
Glycerine	400	320
Industrial Ethanol	408	115
Oils and Resins ***	1,214	550
Activated Carbon	254	220

*Rosin, tall oil, sulfate turpentine

**Regenerated cellulose, cellulose ethers, ethyl cellulose

***Soy oil, peppermint, spearmint, other plant oils

Sources: CMR 2002, DOC-ASM 1999, Corn Annual 2001, Chem Expo 2002, EI 2001.

However, this underestimates the actual value of products containing biomass currently produced in the U.S. For example, the value of adhesives containing bio-ingredients is about $3.3 billion annually [ACC 2002, ILSR 1992]. Biobased inks are valued at about $0.2 billion.

Major producers of bioproducts within several key areas are shown in Table 1-6. Producers of bioproducts from starch and sugar and wood chemicals are comprised mostly of large chemical companies, food processors, and pulp and paper companies. Producers of oil products are most often food processors, although some are multi-faceted conglomerates with subsidiary companies in food, pharmaceuticals, chemicals and biotechnology.

Role of Biomass in the Economy

Biomass is only one of many materials needed to fuel and feed the U.S. economy (see Table 1-7). For example, chemicals manufactured from hydrocarbons (petroleum, natural gas) and mineral resources are used in almost every aspect of life. Metals such as steel and aluminum create our infrastructure as well as consumer goods. Fossil fuels (petroleum, coal and natural gas) are the primary inputs to transportation and power generation. When viewed in the context of all the materials that are important to our quality of life, bioproducts may appear to play a relatively small role in comparison to other materials.

However, biomass is a critical element in many parts of the economy and a staple for human existence and development. Food processors rely on biomass to provide food for people as well as animals in the U.S. and across the globe. Forest industries create paper, packaging, textiles, and a wide diversity of building products from trees and wood residues. Biomass and other renewable resources provide a small but growing share of power production and transportation fuels. Bioproducts have well-established markets in soaps and detergents, pharmaceuticals, industrial chemicals, textiles, fibers and composites.

Table 1-6 Major Producers of Bioproducts

Bioproduct Category	Producers
Starch and Sugar Products	ADM (ethanol, citric acid, sorbitol) Arkenol (ethanol) Cargill (citric acid, sorbitol) Cargill Dow (ethyl lactate, PLA) Cargill Corn Milling (sugar) Minnesota Corn Processors (ethanol) Midwest Grain Products (ethanol) DuPont (1,3-propanediol) Grain Processing Company (ethanol) Tate & Lyle Citric Acid (citric acid) Tate & Lyle - A.E. Staley (starch, ethanol) Williams Bio-Energy (ethanol)
Cellulose	Dow Chemical (cellulose derivatives) Celanese (cellulose derivatives)
Wood Chemicals	Westvaco (activated carbon, wood chemicals) Hercules (activated carbon, wood chemicals) Norit America (activated carbon) Arizona Chemical (wood chemicals) Georgia Pacific (wood chemicals) Akzo Nobel Resins (gum rosin)
Oils and Lipids	Cambrex (caster oil derivatives) Vertec Biosolvents, Inc. (soy products) AG Environmental Products LLC (soy solvents, lubricants) West Central Soy (soy solvents, cleaners, lubricants) Lonza (glycerin, fatty acids)

When viewed in this larger context, a significant portion of our economy *is biobased*, relying on carbohydrates rather than fossil-based hydrocarbons. As illustrated in Table 1-7, the conventional uses of biomass already account for well over $400 billion in products annually. As the manufacture of industrial bioproducts expands into new markets, its importance in the economy is expected to grow far beyond the traditional uses for food, textiles, paper and building materials.

Using biomass to create industrial and consumer products is not a new idea. However, new products are emerging that do not have historical roots in biomass. These new products may compete with and eventually replace a number of products that are now made from petroleum and mineral resources (plastics, glass, metals). The greatest driver for the growth of new markets will be public acceptance of biomass as an integral resource along with petroleum, minerals and other natural resources.

There are many compelling reasons to increase the use of biomass as a resource for industrial products, including the use of imported oil, the environmental consequences of fossil energy use, rural economics, and others. These are described in more detail in the next section.

Table 1-7 Material Inputs to the U.S. Economy

Economic Sector	Processing Energy (Quads)	Feedstock Energy (Quads/yr)	Production/ Capacity (billion lbs)	Gross Domestic Product (billion$)
Inorganic Chemicals	0.9	2.8	294	95
Organic Chemicals	2.8		175	188
Pharmaceuticals			na	110
Soaps, Detergents, Toiletries			na	13
Paints and Coatings			na	18
Lubricants and Greases	0.1	0.4 [a]	20	na
Aluminum, Iron and Steel	2.3	0.8	368[b]	68
Glass	0.2	0	40	17
Pulp & Paper	3.2	6.3[f]	373	109
Food	1.0	2.9	623	298
Feed		1.0[f]	141	
Industrial Bioproducts	na	na	12	8
Transportation Fuels				262[e]
Conventional[c]	3.5	27.7	235 billion gal/yr	
Biobased	na	na	2 billion gal/yr	
Power Generation				247[e]
Fossil Fuel/Nuclear	39.0		776,892 MW	
Renewables[d]	3.4		11,010 MW	
Total	53.2	31.7 (fossil) 10.2 (biomass)	-	1,433

a Estimated based on production volume.
b Does not include products made from purchased steel.
c Includes finished motor gasoline and distillate fuels (diesel).
d Includes biomass, solar, hydroelectric, wind, and geothermal energy.
e Estimates based on average prices over the year.
f Calculated based on higher heating value of biomass feedstocks.
na not available
Sources: DOC-ASM 1999; EIA 2000b; EIA 2000c; EI 2001, EIA AEO 2002.

1.2 Trends and Drivers

Only one hundred years ago our economy was based primarily on biomass, or carbohydrates, rather than hydrocarbons. In the late1800s, the largest selling chemicals were alcohols made from wood and grain, the first plastics were produced from cotton, and about 65% of the Nation's energy came from wood.

By the 1920s, the economy started shifting toward the use of fossil resources, and after World War II this trend accelerated as technology breakthroughs were made. By the 1970s, fossil energy was established as the backbone of the U.S. economy, and all but a small portion of the carbohydrate economy remained. In the industrial sector, plants accounted for about 16 percent of inputs in 1989, compared with 35% in 1925 (Figure 1-2).

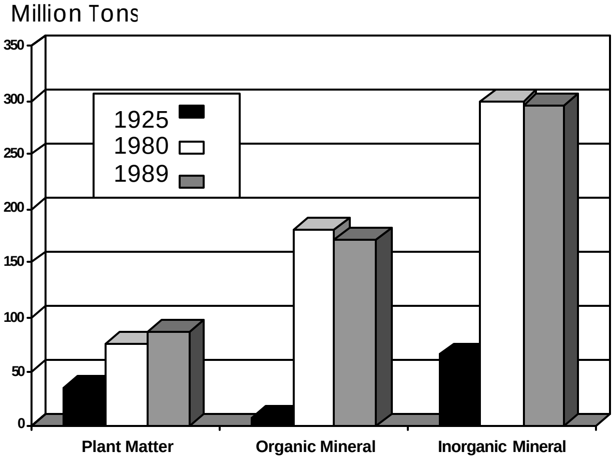


Figure 1-2. Trends in Industrial Materials Use
[ILSR 1992]

Processing cost and the availability of inexpensive fossil energy resources continue to be driving factors in the dominance of hydrocarbon resources. In many cases, it is still more economical to produce goods from petroleum or natural gas than from plant matter.

Technological advances in the biological sciences and engineering, political change, and concern for the environment have begun to swing the economy back toward carbohydrates on a number of fronts. Consumption of biofuels in vehicles, for example, has risen from zero in 1977 to nearly 1.5 billion gallons in 1999. The use of inks produced from soybeans in the U.S. increased by four-fold between 1989 and 2000, and is now at more than 22% of total use [ILSR 2002].

Advances in Technology and Product Development

Technological advances are beginning to make an impact on reducing the cost of producing industrial products and fuels from biomass, making them more competitive with those produced from petroleum-based hydrocarbons. Developments in pyrolysis, ultra centrifuges, membranes, and the use of enzymes and microbes as biological factories are enabling the extraction of valuable components from plants at a much lower cost. As a result, industry is investing in the development of new bioproducts that are steadily gaining a share of current markets.

In the chemicals and food processing industries, companies are developing new technology that will enable more cost-effective production of all kinds of industrial products from biomass. One example is a plastic polymer derived from corn that is now being produced at a 300 million pound per year plant in Nebraska, a joint venture between one of the world's largest grain merchants and the largest chemical producer (Cargill and Dow Chemical) [Forbes 2001].

Other chemical companies are exploring the use of low-cost biomass processes to make chemicals and plastics that are now made from more expensive petrochemical processes (e.g., DuPont's Sorona® polymer precursor, 1,3-propanediol) [Forbes 2001]. Strategic partnerships between the chemical industry, food, textiles and agricultural sectors are expected to become the mainstay of the emerging bioproducts industry and foster its growth over the next two decades.

Dow Chemical, for example, has joined with Universal Textile, a carpet backing supplier, to launch the BIOBALANCE™ polymers line, a soy-based product that can replace a portion of the polyurethane carpet backing that is now the standard in carpet manufacture. This product, developed with funding from the United Soybean Board, can also be used in automotive interiors and other textile applications.

Procter & Gamble, a major producer of glycerine and other bioproducts for use in household products, has formed a "technology council" with Archer Daniels Midland (ADM) to develop new natural products that take advantage of P&G marketing strengths and ADM's biobased raw materials. P&G is also working with USDA to develop a process for producing lauric oil from cuphea, an oilseed that grows in the U.S., rather than from expensive imported tropical oils [C&EN 2002a].

Another trend is the emergence of bioproduct start-up firms in the business of creating innovative bioproducts for niche markets. One example is Vertec BioSolvents, a company that is developing and marketing environmentally-friendly solvents from corn and soybeans on a relatively small scale. Vertec targets solvents that are under regulatory pressure, and is continually expanding into new markets [CMR 2002]. While these firms have an important impact on specialty markets, the producers of larger commodity bioproducts will continue to be the primary drivers for the industry.

The Biorefinery Concept

Biorefineries could be the foundation of the new bioindustry. The biorefinery is similar in concept to the petroleum refinery, except that it is based on conversion of biomass feedstocks rather than crude oil. Biorefineries in theory would use multiple forms of biomass to produce a flexible mix of products, including fuels, power, heat, chemicals and materials (see Figure 1-3). In a biorefinery, biomass would be converted into high-value chemical products and fuels (both gas and liquid). Byproducts and residues, as well as some portion of the fuels produced, would be used to fuel on-site power generation or cogeneration facilities producing heat and power.

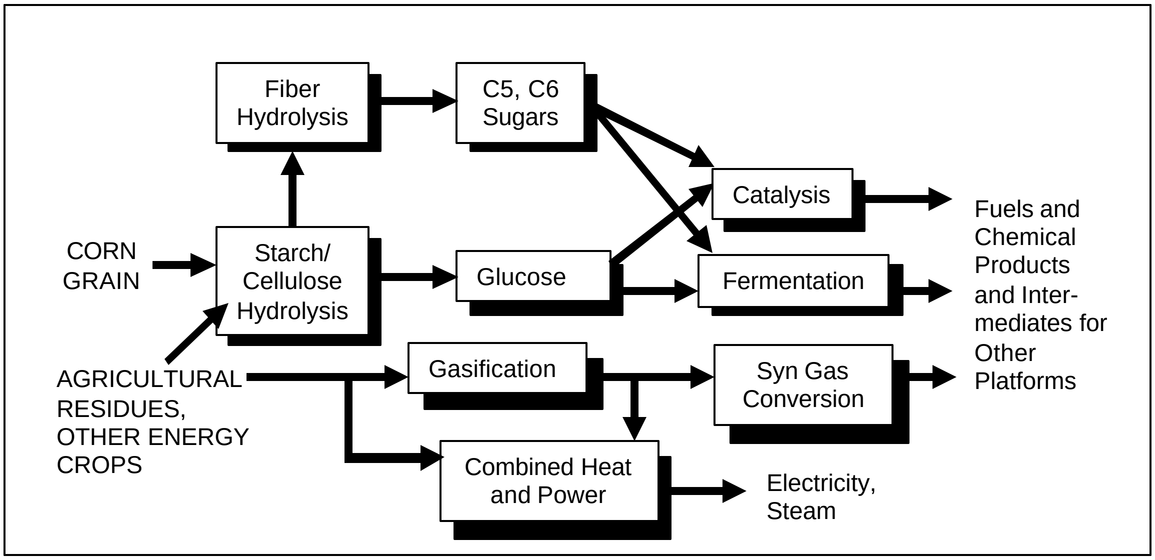


Figure 1-3 The Biorefinery

The biorefinery concept has already proven successful in the U.S. agricultural and forest products industries, where such facilities now produce food, feed, fiber, or chemicals, as well as heat and electricity to run plant operations.

The Archer Daniels Midland complex in Decatur, Illinois, for example, is the prototype for an expanded biorefinery. At this site a large corn wet-milling plant produces industrial enzymes, lactic and citric acids, amino acids, and ethanol. The enzymes are used to convert starch to maltodextrins and syrups, and the chemical products are used in foods, detergents, and plastics. The ethanol is used as a solvent or for transportation fuels. An on-site cogeneration system provides electricity and steam for conversion processes.

Arkenol, a technology development company, is marketing a biorefinery technology based on acid hydrolysis that can produce a variety of biobased chemicals and transportation fuels [Arkenol 2002]. The company is currently developing several biorefineries throughout the world, including a facility in Sacramento, California that will produce 90 million pounds per year of citric acid along with 4 million gallons of fuel ethanol.

The new starch-based Cargill Dow PLA facility discussed previously is a good example of an emerging biorefinery. Cargill Dow is also exploring the use of lignocellullosic biomass such as corn stover or wheat straw to produce lactic acid, PLA, ethanol and other industrial products. Residual biomass can be used to generate power.

The biorefinery concept has long been in place in the pulp and paper industry, where wood is converted into pulp for papermaking, and various byproducts are used to produce chemicals, fibers and plastics. Black liquor, a byproduct of the pulping process, is used in on-site cogeneration systems to meet a large share of electricity and steam requirements for the plant.

Biorefineries offer the most potential for realizing the ultimate opportunities of the bioenergy industry. However, flexibility will be a key factor in maximizing the economic viability of the biorefinery concept. Ideally, the biorefinery would have the capability to vary feedstock inputs and process streams to create on-demand product slates, much like petroleum refineries do today. High-value products may represent only 20% of production, for example, yet account for 80% of profits. By operating with a highly flexible and profitable product output, the biorefinery will be able to get the most value from a bushel of biomass, while optimizing overall profitability.

Government Policy and Legislation

Government policy has been motivating the use of biomass in various ways for decades, beginning in the early 1970s. Over the last ten years legislators have recognized the potential of biomass to supplement our energy resources and have passed several important laws aimed at encouraging the growth of the bioindustry.

The **Energy Policy Act of 1992 (EPAct)** grew out of the previous Bush Administration's efforts to establish a national energy policy. Under Title XII, EPAct provided appropriations for projects in biobased fuels and power systems, including conversion of cellulosic biomass to fuels, ethanol manufacture, and direct combustion or gasification of biomass.

More recently, Congress passed the most important piece of legislation to emerge in support of the newly evolving bioindustry – the **Biomass R&D Act of 2000**. The Act directs the U.S. Departments of Energy and Agriculture to

Major Legislative Actions Impacting Bioproducts

- *Energy Policy Act (EPAct) 1992*
- *Biomass Research & Development Act of 2000*
- *National Energy Policy (NEP) 2001*
- *Farm Bill 2002*

integrate their efforts to foster a domestic bioindustry through focused R&D programs. Research is funded under *Section 307, Biomass Research and Development Initiative*. The objective of the Initiative is to develop the next generation of cost-effective, sustainable technology for biobased fuels, chemicals and power.

Most recently, the passage of the **2002 Farm Bill** demonstrates continued legislative support for the development of the bioindustry. For the first time in history, the 2002 Farm Bill contains an Energy Title, with five programs providing mandatory funding for bioenergy activities.

The Farm Bill reauthorizes the Biomass R&D Act of 2000, continues funding for biomass R&D programs, and authorizes grants for the development of biorefineries. The Bill also mandates the purchase of biobased products by Federal agencies when practical, a step that could provide added market incentives for cost-competitive bioproducts. Overall, the 2002 Farm Bill sends a clear message that biomass is a viable energy alternative to be explored and promoted.

The efforts of the current administration to develop an energy plan will have important implications for the bioindustry. The **National Energy Policy (NEP)** report, commissioned by President Bush in 2001, reviews the Nation's energy situation and presents a strategy to achieve a reliable energy structure that will support our quality of life and still maintain protection of the environment.

The increased use of renewable energy, including biomass, is an integral part of the NEP strategy and provides further justification for research in this area. The Executive Branch is now working with Congress to enact a National Energy Policy which will provide future guidance and support for bioenergy.

National Security

The increasing scarcity and cost of fossil resources are contributing to a growing interest in bioproducts. Biomass can potentially be used to diversify our current fossil-energy based systems for fuel, power and products. Diversification can reduce our vulnerability to disruptions in energy supply as well as our dependence on imported energy sources for both fuels and important consumer products.

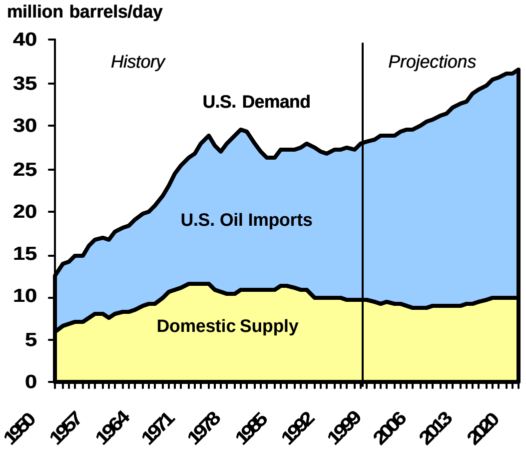


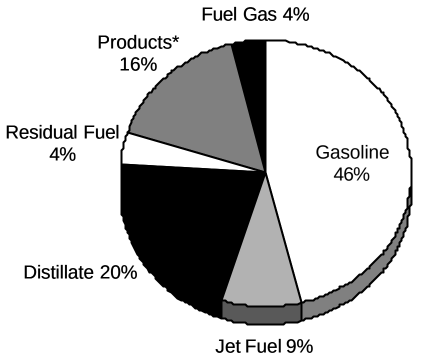
Figure 1-4 Trends in U.S. Oil Supply and Demand [EIA AEO 2002]

The amount of oil imported into the U.S. has been steadily rising over the last ten years (see Figure 1-4). Today, imports constitute 65.5% of the U.S. oil supply, which is 15% higher than import share in 1973 prior to the oil crisis and embargo. In the aftermath of September 11th, the increasing dependence of the U.S. on imported oil has become a pressing issue of national security.

Transportation fuels account for a large share of the use of petroleum in the U.S. (see Figure 1-5). However, a significant amount (nearly one billion barrels of oil equivalents) is used annually to produce industrial chemicals and materials [ACC 2002, EIA AER 2001]. These products are an integral part of the U.S. economy, and are used to manufacture plastics, paints, paper, textiles, pharmaceuticals, building materials, and a host of other goods.

The Nation is more than dependent on oil for transportation fuels – oil provides the basic building blocks for virtually every product we use. Supplementing petroleum resources with biomass for production of industrial and consumer products could make a significant impact on oil imported for this purpose.

The biorefinery represents one very viable part of the solution for the imported oil problem. These highly flexible facilities have the potential to profitably manufacture the many products that now come from petroleum. Biorefineries could help meet demand for both transportation fuels and critical consumer products, with fewer environmental impacts.



* Petrochemicals, LPG/NGL, waxes, lubricants, asphalt

Figure 1-5 Uses of Petroleum in the U.S.
[EIA AER 2001]

Regulatory Drivers and "Green" Consumerism

Environmental regulations governing the wastes and emissions related to hydrocarbon-based products have encouraged the use of some bioproducts. Government incentives to make "cleaner" products or regulate "dirtier" products can motivate market changes that favor production of bioproducts. Banning the use of non-degradable plastic bags for yard waste, for example, has made some starch- and sugar-based plastics more competitive with those produced from petrochemical feedstocks.

Regulations that ban the use of materials such as phosphates in detergents, or synthetic dyes in foods, have opened up new markets for more benign materials made from plants. Regulations governing the amount of volatile organic compounds (VOCs) that can be released from printing operations have encouraged most U.S. newspapers to use soy-based inks in some part of their operations.

Global warming is another area where regulatory as well as policy changes could support the use of biomass as an industrial input. Biomass is carbon-fixing, and represents a way to produce fuels, products and power with a 'net-zero' contribution to global warming. Although no regulations have been passed requiring mandatory reductions in greenhouse gases, a key component of the Bush administration's new climate policy is to reduce U.S. greenhouse-gas intensity by 18% over the next decade through voluntary means. As a result EPA has launched the "Climate Leaders" program, a voluntary partnership with industry to reduce greenhouse-gas emissions [EPA 2002]. These and future efforts to reduce greenhouse gases could bolster the use of biomass as an energy resource.

Along with government regulation, environmental consciousness has created "green consumerism," where a segment of consumers are willing to pay more for products that are less harmful to the environment. Today many of these "green" products are biobased (household cleaners, organic fertilizers, soy-based lubricants, plastics).

Rural Development

The impacts of the bioindustry on rural economies have yet to be quantified, but could be very positive. Development of a bioindustry will require an increase in production and processing of biomass, and could provide a boost to rural areas. It could create new cash crops for farmers and foresters, many of whom currently face economic hardship. Development of a larger bioindustry would require new processing, distribution, and service industries.

These would need to be located in rural communities close to the feedstock and could potentially result in positive impacts on rural economic growth.

As the bioindustry becomes established, agricultural and forestry industries would go beyond traditional roles of providing feedstocks for food, feed and fiber, and become an integral part of the transportation and industrial supply chain. New biorefineries, as well as expansion of existing biorefineries, will be central to the growth of the rural economy.

Genetic Engineering of Crops

An issue that affects all sectors of the bioindustry is controversy surrounding the use of genetically modified (GM) crops and their impact on ecology and human health. The controversy centers around seeds that have genetically-altered input traits, i.e., those leading to improved crop yields (herbicide and pest-resistant, tolerance to drought, heat or cold).

There are tremendous advantages to using GM seeds, including improved yields and reduction in the use of chemical crop protection. Use of GM pest-resistant cotton, for example, has reduced the use of broad spectrum pesticides by one million gallons since commercial introduction in 1996 [CMR 1999].

In addition, genetic engineering is producing seeds that grow plants with additional oil content or other functional characteristics (output traits) that could be important to feedstock plants. DuPont and Pioneer Hi-Bred International are collaborating on a large scale to produce seeds with improved output traits, such as nutrition and oil content [CMR 1999].

Regulatory barriers and public uncertainty have made market approval difficult to obtain for GM crops in Europe, but other regions are more accepting (e.g., South America). Some countries have banned or are discouraging the import of GM crops. Japan, for example, one of the largest buyers of U.S. wheat, has said it will buy from other sources if the U.S. cannot guarantee biotech-free wheat [C&EN 2001a]. Some European consumers are uncertain about the safety of biotech foods and crops, and want strict labeling laws that would apply not just to food and crops but derived products such as starch and oils. In the U.S., most processed food has some ingredients derived from biotech crops [C&EN 2003].

The European Union (EU) is now developing legislation that will require all biotech foods and products derived from them to be labeled and traceable from the farm to the consumer (exact strains of the GM crop must be listed). The U.S. food industry has taken the position that such legislation will make it nearly impossible to sell biotech food or feeds in Europe. In response, the U.S., along with Egypt, Argentina and Canada have lodged a formal complaint with the World Trade Organization [C&EN 2003].

Despite the controversy, use of GM seeds continues to expand in the United States (see Figure 1-6). In June 2001 the USDA reported that the combined planting of GM corn, cotton and soybeans increased by 18% to about 82 million acres, exceeding government projections. Biotech seed accounted for 26% of corn, 69% of cotton, and 68% of soybean acres [C&EN 2001a, CMR 2001c, CMR 1999].

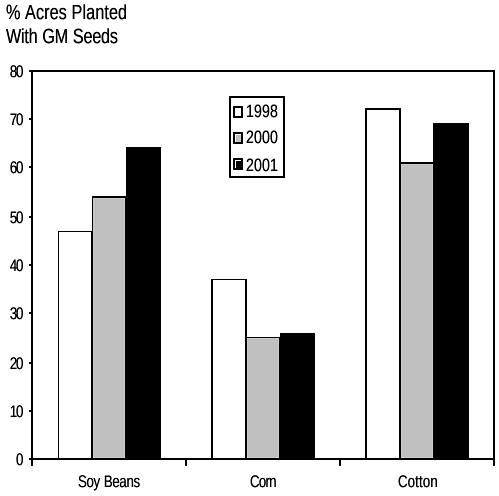
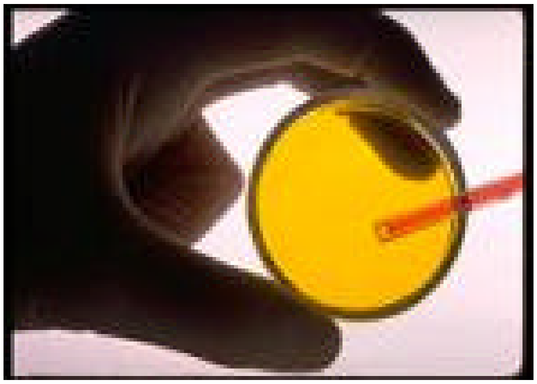


Figure 1-6 Trends in the Use of Genetically Engineered Seeds in U.S. Farm Production

The future for genetically engineered crops is still uncertain. Some countries continue to approve new GM crops. Once labeling legislation is in place, the EU could potentially begin approving GM crops and products. Approval, however, does not guarantee crops will be grown or marketed. A number of GM crops such as herbicide-tolerant sugar beets, flaxseed and potatoes have been approved in the U.S. but are not being grown because they have been rejected by major buyers [C&EN 2003].

Biotechnology has the potential to yield tremendous economic advantages through the use of GM seeds. With GM seeds it is possible to reduce feedstock costs, improve sustainability and reliability, and manipulate the components of plants to produce the most desirable products. This can also be accomplished through conventional plant breeding, but will take much longer and be more costly.

GM seeds could be an important factor in establishing the reliable feedstock supply needed for future bioproduct markets. To continue progress in this area, both the public and private sectors will need to address the potential impacts of GM crops on the environment and human health.



Future Outlook

Today, hydrocarbons still dominate the U.S. economy. Although exact numbers are not available, it has been estimated that plant matter currently provides about 7% of inputs to organic chemical products (by weight), with another 3% used for transportation fuels and power [EI 2001].

However, promoting the use of biomass as an energy resource continues to command strong bipartisan support. In the *Vision for Bioenergy and Biobased Products in the United States*, published by the Biomass Technical Advisory Committee under the Biomass R&D Act of 2000, a goal was set to produce 12% of chemicals and materials from biomass in 2010, 18% in 2020, and 25% in 2030, compared with the 5% produced today [Vision 2002].

Industry is already forging ahead with new bio-ventures. With current momentum, shipments of bioproducts could quadruple over the next 20 years to over 60 billion pounds per year. The demand for corn-derived chemical products alone is predicted to grow at a rate of 13.4% per year, with a gain in market value of 22% annually [Corn Annual 2001].

The impetus for new bioproducts will continue to come from favorable government policies, the implementation of biorefineries, and the need to reduce the use of imported oil. Technology development, as well as federal support for fundamental and applied R&D, will be critical in accelerating product development. Perhaps the greatest factor driving the growth of bioproducts will be acceptance by the public, business enterprises, and government that biomass can provide a solution to some of our most pressing resource problems.

The potential for bioproducts to move into entirely new and non-conventional markets is substantial. Much like the phenomenal movement of plastics since their widespread introduction in the 1970s, new bioproducts with improved performance could make significant inroads in markets historically dominated by other materials. Not only can entirely new plastics be created from biomass, but innovative industrial materials with a range of uses from consumer products to infrastructure. To make significant inroads, however, bioproducts will need to be environmentally sound and cost-competitive with traditional products.

1.3 Energy Impacts

Feedstock Energy Potential of Biomass

Biomass has potential energy value both as a fuel (for heat and power) and as a feedstock (energy value of raw material used for production of a chemical or material). The biomass resources (assuming variable feedstock types) that are available for use represent about 6-10 quadrillion Btu (quads) of energy [ORNL 1999, ADL 2001].

In 2001, the fossil-based feedstock energy used in the production of chemicals was about 3.2 quads [ACC 2002], which is equivalent to over 700 million barrels of oil. This includes feedstocks for organic chemicals, plastics, synthetic rubber, non-cellulosic fibers, and ammonia-based fertilizers. In the petroleum refining industry, over 3.6 quads served as the feedstocks for many non-fuel products, including petrochemicals, waxes, lubricants, and tar. Over 55% of feedstocks used at refineries for non-fuel products go into the production of petrochemicals that are sold to the chemical industry as intermediates for plastics and other products [EIA 2001].

As Table 1-10 shows, there are significant opportunities for biomass to supplant the fossil-based feedstocks used in both the chemicals and petroleum industries. The total feedstock energy that could be impacted is over 7 quadrillion Btu, with 88% of this being petroleum-derived. [EIA 2001].

Hydrocarbon feedstocks represent the largest share of raw materials purchases in the chemical industry, nearly $24 billion annually (see Figure 1-7). By comparison, purchases of agricultural commodities by the chemical industry for conversion into products was about $4.5 billion in 2001 [ACC 2002].

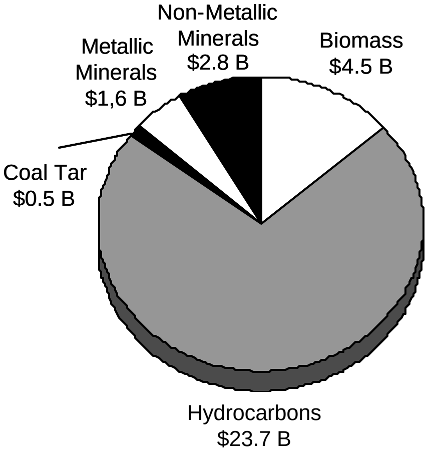


Figure 1-7 Raw Material Purchases Associated With the Chemical Industry
[ACC 2002]

Processing Energy

Energy is an important factor in production of chemicals and materials, whether the feedstock is fossil energy or biomass. Breaking down fossil feedstocks into the desired products requires high pressures and temperatures, resulting in the consumption of large amounts of heat and power. In contrast, the bonds of plant materials are easier to break, and many bioconversions occur at or near room temperature, atmospheric pressures, and neutral conditions. The result in some cases is lower energy requirements for conversion of feedstock to products.

In today's bioprocesses, energy is required for preparation of the feedstock, separation of products, cooling and drying operations, and machine-driven equipment (mixers, grinders, conveyors, pumps, compressors). About 90% of the energy consumed in production of bioproducts is fuel (natural gas, coal, oil) used primarily for process heating and cooling.

Biomass and the products of biomass processing can also be used to generate power and heat for manufacturing processes. In the biorefinery concept, byproducts that are difficult to convert to chemicals or materials could be used as a process energy resource.

Table 1-8 illustrates the relative use of process heat and power and feedstock energy in the basic materials industries. The chemicals and petroleum refining industries represent the most energy-intensive of the basic industries.

According to the Manufacturing Energy Consumption Survey (MECS) selected sectors of the bioproducts industry consumed about 118 trillion Btu of energy in 1994, including electricity losses (see Figure 1-8) [MECS 1994]. Natural gas accounts for the largest share of energy use.

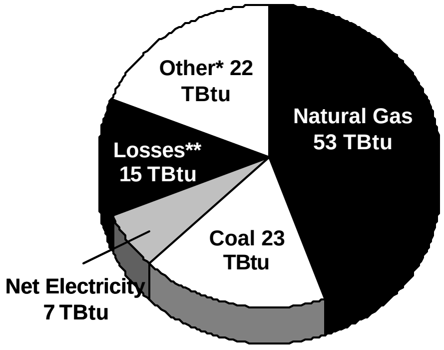
Table 1-8 Energy Use Requirements for Basic Materials and Chemicals Manufacture, 1998 (trillion Btu)

Material	Process Energy Use	Feedstock Energy
Organic Chemicals and Plastics	2,261	2,412*
Inorganic Chemicals	1,443	360*
Food & Feed	1,044	3,903**
Pulp & Paper	2,744	6,300**
Petroleum Refining	3,622	3,748*

* Liquefied petroleum gases (LPG), heavy petroleum liquids, natural gas, coal, minerals
** Biomass energy, based on higher heating value
Source: MECS 1998

Energy costs can be a significant factor in the economics of producing industrial bioproducts, just as they are for conventional chemical products. Energy expenditures for the bioproducts sectors reporting (wet corn milling, cellulosic fibers, gum and wood chemicals, soybean processing) were about $377 million in 1999, which represents about 5% of industry sales for those sectors. The energy intensity of various products sectors is shown in Figure 1-9 [DOC-ASM 1999]. On a Btu/dollar of shipments basis, cellulosic fibers, ethanol production, and wet corn milling (which produces feedstocks for ethanol and other industrial bioproducts) are the most energy-intensive.

Optimizing the use of processing energy could be a defining factor in making some bioproducts competitive with fossil-derived counterparts. Volatilities in energy price and supply, such as rising natural gas prices, will affect biobased as well as fossil-based products.



Total Energy Consumed (with Electricity Losses) 118 Trillion Btu

Figure 1-8 Energy Use by Fuel Type in Selected Bioproducts Sectors [MECS 1998]

* Includes oil, byproducts, renewables, and a small amount of feedstock energy.
** Losses incurred during the distribution, generation and transmission of electricity from off-site utilities.

Note: Represents energy consumed in four NAICS sectors: Gum and Wood Chemicals, Cellulosic Fibers, Wet Corn Milling, and Soybean Oil Processing.

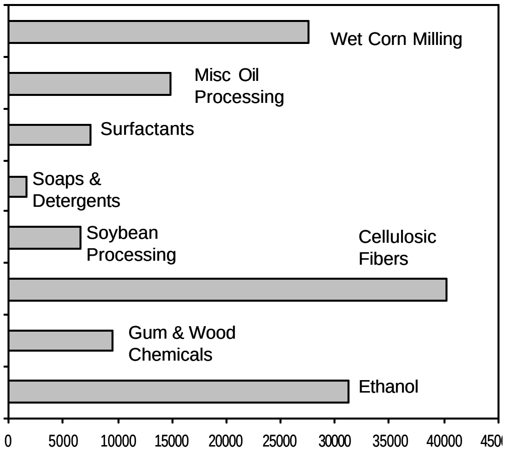


Figure 1-9 Energy Intensity in Selected Bioproducts Sectors [DOC ASM 1999]

1.4 Environmental Issues

Bioproducts have gained momentum in some cases due to the perceived "green" advantages of using biomass rather than fossil energy for production of chemicals and industrial products. Another key benefit in the move toward bioproducts is the potential for reducing pollutants emitted to the environment from fossil-based chemical processes.

Pollution associated with the manufacture of chemicals and industrial products from fossil resources can impact air, water and land. Some of these pollutants are hazardous and/or toxic, and have short- and long-term impacts on human health and safety. When comparable bioproducts are produced, the environmental impacts are sometimes less or eliminated.

Emissions to the Air

Air pollution is generated in chemical or bioconversion processes during the combustion of fossil fuels in process heaters and boilers, and is released as sulfur dioxide (SO_x), nitrogen oxides (NO_x), particulates (PM10 and PM2.5), volatile organic compounds (VOCs), carbon monoxide (CO), and carbon dioxide (CO_2).

Since many bioconversion processes occur at or near room temperature, atmospheric pressures, and neutral conditions, there are often lower combustion energy requirements and fewer associated emissions than conventional chemical processing. However, energy used for feed preparation, drying and product separations can be a significant source of combustion emissions, which can be partially offset by the use of renewable fuels to meet processing energy demand.

During chemical processing harmful volatile compounds may be released from point sources and as fugitive emissions from valves, vents and pipes in the manufacturing plant. While bioconversion processes are often more benign, they can also release fugitive emissions. Soybean oil extraction, for example, requires the use of volatile solvents (e.g., hexane). While virtually all the hexane is recycled, fugitive emissions of hexane can be released during the process. In wet corn milling, sulfur dioxide is added to the batch and can be responsible for volatile releases during processing. While these releases are controlled through filtering systems, fugitive releases can still occur.

A primary concern for impacts on air from bioprocesses is particulate emissions, which are generated during grain crushing and grinding operations where the feedstock is prepared prior to conversion to products. Most of these particulates are controlled using baghouses or filtering systems such as those used in grain storage and processing [Sources: EPA 1995, EPA 2001].

Solid and Liquid Wastes

Many chemical processes require large quantities of aromatic solvents or strong inorganic acids and bases (e.g., sulfuric acid, sodium hydroxide) that can result in effluent streams that are harmful to the environment. These can be liquid effluents, contaminated wastewater, or solid wastes, and must be recycled or treated and disposed of.

One of the most attractive aspects of bioproducts is the potential to reduce the generation of hazardous and toxic wastes associated with the manufacture of fossil-based products. Most biological processes require natural catalysts (e.g., enzymes) and solvents (water) and produce few or no toxic or hazardous byproducts. In most cases, solid wastes and effluents from these processes are biodegradable or can be recycled or disposed of without excessive treatment processes.

However, not all bioprocessing is benign. One example is the production of cellophane (cellulose acetate) which is used to make film and other products. The feedstock for cellophane (purified alpha cellulose) comes from sulfite pulp mills, where 5-6 pounds of polluting effluents are generated for every 100 pounds of cellulose acetate [ILSR 1994]. Chemicals such as acetic acid, acetic anhydride, sulfuric acid, hypochlorite bleach, magnesium acetate, and acetone are also used to manufacture the final cellophane product.

Processing steps using these chemicals result in volatile emissions and high-acid waste water. However, when compared with similar fossil-based products such as polyvinyl chloride or polyurethane, the pollution generated by the cellophane process is 2-3 times less. Some of the chemicals used to make cellophane could be replaced with biobased chemicals (bio-derived acetic acid and acetic anhydride, biosurfactants), which would make the cellophane process more environmentally benign.

Global Climate Change

Greenhouse gases (carbon dioxide, methane, nitrous oxide) that may contribute to global warming are generated through combustion of fuels, including biomass fuels, and are also byproducts of some chemical reactions (ammonia synthesis, soda ash manufacture). When petroleum is used as the feedstock for a chemical or plastic, about 75-80% of the feedstock carbon is sequestered in the product [EIA 2002b].

Using plants as a feedstock instead of petroleum or natural gas can potentially reduce the amount of carbon dioxide emitted to the atmosphere. Plants sequester carbon via photosynthesis. Globally, about 62 gigatons of carbon are taken-up by plants annually via the photosynthesis process [Johnston 1999]. Respiration, which occurs in living things and through plant-matter decay, produces about 60 gigatons of carbon which is released back into the atmosphere. The net uptake by plants is about 1-2 gigatons, and is a small fraction of the uptake of CO_2 in the atmosphere. Plants are a carbon sink, and activities which reduce plant matter, such as deforestation, increase carbon dioxide in the atmosphere.

Producing chemicals and industrial products from biomass directly reduces the associated carbon released during production of fossil-based products and increases carbon-fixing plant matter. It has been reported that the potential for reducing carbon through substitution of bioproducts is about 3.5 MMTCE (million metric tons of carbon equivalents) by 2010 [CCTS 1997]. Carbon is also sequestered for a relatively long period of time in the bioproduct before it is released into the atmosphere through biological decay.

2.0 Agriculture and Forestry Resources

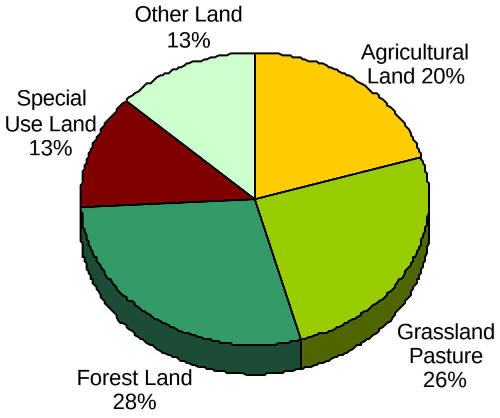
To compete with the conventional chemical products industry based on fossil and mineral resources, the bioproducts industry will need a reliable, cost-effective raw materials infrastructure. Our indigenous biomass resources are considerable, as the following discussion will illustrate. There is also great potential to increase these resources through technological, political and social change. However, numerous factors must be optimized to create favorable economics for the use of biomass as a resource for bioproducts.

The cost-effectiveness of agricultural and forestry production practices, as well as the efficient storage and transport of harvested biomass resources will be critical elements. Environmental impacts and sustainability are also issues that must be incorporated.

2.1 Biomass Resources

Current production data for agricultural crops are shown in Table 2-1, in descending order according to planted acres. Corn, soy, wheat, and cotton currently dominate planted cropland in the U.S., and account for over $42 billion in production value annually. Today corn and soybeans are the largest biomass resources for industrial products. About 940 million bushels of corn and 3.4 billion pounds of soybeans are used annually for this purpose [USB 2001].

Forestry and rangeland are abundant in the U.S., and provide some of the biomass resources in use today. Within our domestic boundaries forest lands alone total more than 642 million acres. Another 580 million acres are used for grassland pasture (see Figure 2-1).



Total Domestic Land: 2.263 million acres

Figure 2-1 Land Resources in the United States, 2000 [USDA NASS 1997]

Table 2-1 Production and Market Statistics for U.S. Cropland, 2000

Crop	Planted (1000 acres)	Harvested (1000 acres)	Bushels/ Acre	Production (MM bushels)	Average $/Bushel	Annual Value (MM$)
Corn	74,545	72,732	137.1	9,968	1.85	18,621
Soy	74,496	72,718	38.1	2,770	4.75	13,074
Wheat	62,529	53,028	41.9	2,223	2.65	5,970
Cotton	15,537	13,098	631	8,265	0.58	4,777
Sorghum	9,195	7,723	60.9	470	1.75	823
Barley	5,844	5,201	61.1 (lb/acre)	318	2.15 ($/lb)	632
Oats	4,477	2,324	64.2	149	1.05	165
Rice	3,065	3,039	6,281(lb/acre)	191 (MM cwt)	5.75 ($/cwt)	1,073
Sunflower	2,792	2,629	1,363 (lb/acre)	3,584	6.45 ($/cwt)	241
Rye	1,335	302	28.5	8,619	2.49	21
Cottonseed	na	na	30.7	402	1.7	677

Note: cwt = hundred weight = 100 pounds; lb = pounds; MM = million
Sources: USDA-NASS 2001, data for 2000; USDA-NASS 2001b

Potential Biomass Resource Base

There are significant additional biomass resources that could be tapped to provide feedstocks for industrial bioproducts. In most cases, these resources represent biomass that is currently either wasted or used in a low-value or relatively unproductive way.

Agricultural crop residues represent one of the largest and most viable largely untapped biomass resources. These include the parts of the crop that are not normally used for food, such as stalks or stems. Major residue sources are corn stover, wheat and rice straw, and cotton stalks. Today these residues are tilled into the field after harvesting to protect the soil, used for animal feed or bedding, and sometimes discarded or burned.

Other waste products, such as the organic solids of municipal waste and wood wastes from construction activities represent a large source of carbohydrate feedstock. These wastes are currently landfilled and put significant demand on landfill capacity. Wastes such as manure, or gases produced at landfills and in anaerobic digesters could also potentially be used to create bioproducts.

Energy crops such as switchgrass or fast-growing trees like hybrid poplar and willow have significant potential for use in bioproducts and bioenergy. These crops can often be grown in less fertile areas where many agricultural crops will not thrive.

Residues from forest thinnings, as well as residues from pulp and paper mills, could provide a small but significant additional resource for bioproducts. Use of forest thinnings could help to reduce the danger of forest fires, while making use of mill residues can reduce the amount of mill wastes that must be treated and disposed of.

Figure 2-2 depicts biomass resources beyond what is used to meet demand for food and feed, and represents today's agriculture productivity levels. With the rapid advances being made in biotechnology, resources could be increased by 2-3 fold in 10-30 years. Corn productivity alone has increased by about 1.5% per year with conventional breeding over the past decade.

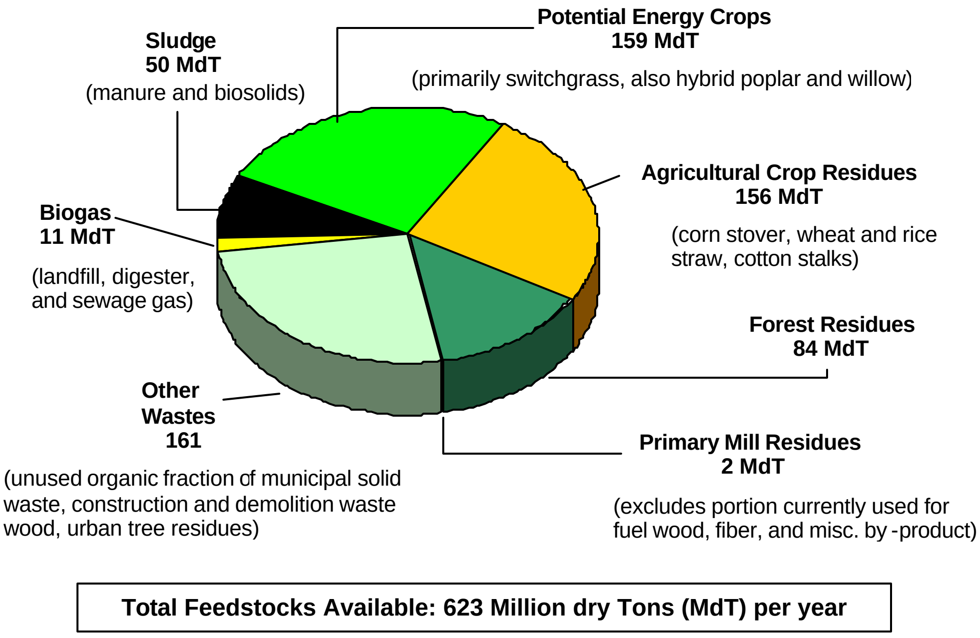


Figure 2-2 Additional Domestic Biomass Resources Available for Feedstock Uses
[ADL 2001]

2.2 Impacts of Agricultural Practices

Today's agribusiness is far more complex than it was 50 year ago. Crop and forestry production is a balancing act that involves optimizing the use of fertilizers, herbicides and pesticides, minimizing water use, effectively managing field and forest residues, and sometimes incorporating genetically modified seeds and plants. All of these elements impact production costs and ultimately, cost-competitiveness as a resource for bioproducts.

Production practices in agriculture and forestry also impact the availability and quality of the feedstock supply. For biomass to supplement the use of petroleum as a feedstock for industrial bioproducts, the biomass supply must be reliable, of consistent quality, and cost-competitive.

Unlike petroleum, biomass production is greatly impacted by changes in the weather, water availability, soil conditions, fires and other natural disasters, insect populations, and botanical diseases. Today farmers and forest managers address these issues in a variety of ways, such as the use of irrigation, soil enhancers, or agricultural chemicals.

Current practices may or may not be sufficient to effectively sustain the volume of feedstocks that will be required for dedicated industrial products manufacture. New production, harvesting and storage technologies, as well as genetic engineering of seeds or trees to produce superior species may be needed to support the feedstock infrastructure required for a new bioindustry.

Fertilizer Use

Fertilizer application is an important issue in the development of biomass as a sustainable and cost-competitive feedstock. Fertilizers add to the cost of feedstock production, and have environmental and ecological impacts as well (see Section 2.4).

Crops and forests are grown in a variety of climatic and soil conditions, and the use of fertilizers varies accordingly. Fertilizer application also depends on the sophistication and size of the farming operation and practices (irrigation, crop rotation). The average application of fertilizers in crop production is shown in Table 2-2. The purchase and application of fertilizers represents about 5-7% of farm production expenditures, and cost U.S. farmers about $10 billion in 2000 [USDA 2000b].

Table 2-2 Fertilizer Use in Production of Major Crop Resources

	Corn	Wheat	Soy
% Land Receiving Nitrogen	88.6%	79.8%	17.8%
Average Application (lb/acre)	133.0	68.3	20.2
% Land Receiving Phosphate	73.9%	54.9%	24.9%
Average Application (lb/acre)	54.4	33.1	45.1
% Land Receiving Potash	61.3%	19.8%	26.8%
Average Application (lb/acre)	80.5	39.2	77.8
Total lbs/acre	**267.9**	**140.6**	**143.1**

Source: USDA 2000b

Fertilizers are occasionally introduced in forestry management to reduce the mortality of tree species, improve forest production, and favor a particular species. Many forest sites never receive any chemical treatment, and those that do are treated only two or three times during a tree rotation cycle (40 to 120 years) [EPA 2002b].

Fertilizer delivery has improved considerably over the last decade, but advances in technologies such as biologically released fertilizer and real-time geographic matching of fertilizers to plant requirements still require significant research. As the future biomass feedstock infrastructure is developed, new technologies such as genetic engineering of seeds to produce high yield crops and environmentally-benign fertilizer methods could be critical to the cost-effectiveness of the biomass supply infrastructure.

Pesticides, Herbicides and Fungicides

Minimizing the use of agricultural chemicals could have a positive impact on the economics of biomass-to-bioproducts. The cost to purchase and apply pesticides, herbicides and fungicides on domestic farms totaled about $8.5 billion in 2000, or about 5-7% of farm expenditures [USDA 2000b]. The largest per acre application of pesticides and herbicides is corn production -- also a primary resource for today's bioproducts.

Pesticides, herbicides and fungicides are used to cost-effectively control weeds, insects, mites, fungi, nematodes and other species that may threaten the yield, quality or safety of the crop. Annual use of pesticides on crop farms is over 800 million pounds [EPA 1995]. Pesticides are used in forest management (although infrequently) to control insects, improve forest production, reduce tree mortality, and favor certain species. Like fertilizers, applications of pesticides in forestry may occur only two-three times in a tree rotation cycle over a period of 40 to 120 years [EPA 2002b].

Most agricultural chemicals are organic chemicals produced from petroleum feedstocks. The average application of chemicals to major crops is shown in Table 2-3 [USDA 2000b]. The environmental and safety issues connected with the application of chemicals points to the advantages of reducing the use of pesticides and herbicides over the long term. Environmental impacts are discussed in Section 2.4.

Farmers are increasingly turning to genetically modified seeds that can reduce the use of chemicals while increasing yields and crop performance (see Sections 1.2 and 2.4) manufacturing on a large scale. GM seeds and other methods for reducing the use of agricultural chemicals could help to drive down the cost of producing biomass that is dedicated to the manufacture of industrial bioproducts or bioenergy.

Table 2-3 Herbicide and Pesticide Use in Production of Major Crop Resources

	Corn	Wheat	Soy
% Land Receiving Pesticides	26.0%	na	1.6%
Average Application (lb/acre)	0.5	na	0.3
% Land Receiving Herbicides	88.5%	54.7%	90.6%
Average Application (lb/acre)	2.3	0.5	1.1
Total lbs/acre	**2.8**	**0.5**	**1.4**

na not available
Source: USDA 2000b

Irrigation

Irrigation and water availability will be a cost factor in establishing reliable supplies of some biomass feedstocks for industrial use. Industrial end-users of biomass will need assurance that cost risks due to drought and other water availability issues are minimized. Some crops rely heavily on irrigation, and more so in years of drought.

Irrigation is an important factor in the production of crops in some regions of the United States. Irrigation trends for major crops are shown in Figure 2-3. Corn production consumes the most water per year for this purpose. Average water use for selected crops is shown in Table 2-4.

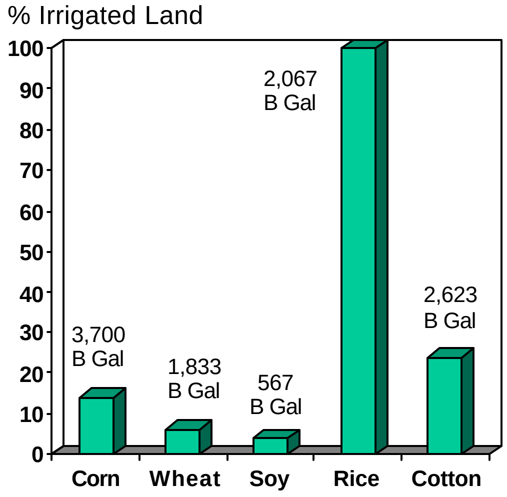


Figure 2-3 Percent of Irrigated Land for Major Crops, 2000 [USDA 2000a]

Table 2-4 Water Use for Selected Crops, 1996

Crop	Gal/ Planted Acre	Gal/ Bushel
Corn	46,537	339
Soy	9,136	240
Wheat	24,240	579
Rice	733,213	117 (per lb)
Barley	75,265	1232 (per lb)
Sorghum	31,375	515
Cotton	138,490	220

Source: USDA 2000a, USDA-NASS 2001, USDA-NASS 2001b

In the future, water use could be reduced through more sophisticated irrigation and land management techniques, or through crops genetically engineered to resist drought conditions. Alternatively, improved irrigation and water management techniques could be applied to increase overall biomass resources by making it possible to utilize arid and semi-arid regions for productive agriculture.

Tillage and Residue Management

Tillage, which is the practice of turning the unused portion of the crop (residues) into the soil, is another factor in crop production economics. Intensive tillage methods can lead to reduction of soil organic carbon, which is important for soil fertility and water retention. Plowing residues into the soil requires fuel, and also increases the need for fertilizers (nitrogen). Both add to production costs.

Farmers are increasingly turning to no-till or other conservation tillage practices which leave more residuals on the ground. Residual cover is needed to reduce wind and water erosion as well as nutrient run-off. However, excess residues left on the soil can lead to problems such as delayed germination of the next crop, excessive weeds, pests and toxins, additional fertilizer and chemical requirements, and restricted water flow in irrigated fields [Glassner 2000, Johnston 1999].

Crop residues have value as lignocellulosic feedstocks for the production of industrial products (see Section 3.2). Although residues are required to protect against erosion, some could be removed with no detriment. More productive use of residues could reduce cultivation costs as well as the organic carbon lost from the soil, while providing a new feedstock source for chemicals and materials.

Tillage Practices

Conventional tillage- (intensive-till) leaves less than 15% of the soil surface covered with crop residue.
Reduced tillage - leaves 15 to 30% of the ground covered by crop residues
Conservation tillage - (no-till, ridge-till, mulch-till) leaves 30% or more of soil surface covered by crop residues.

2.3 Energy Use in Biomass Production

Energy used for the production, storage and transportation of biomass feedstock can impact the economics and cost-competitiveness of biomass as an alternative to petroleum. Energy use issues also affect the ultimate sustainability of biomass as a feedstock.

Crop production requires energy for

- planting and harvesting;
- application of fertilizers, pesticides, herbicides, and fungicides;
- irrigation of land;
- drying and conveying of harvested products on-site; and
- transportation of products to the plant gate.

Indirect energy use associated with agricultural production includes energy consumed in the manufacture of fertilizers, pesticides, herbicides and fungicides in the chemical industry.

Trends in Agriculture-Wide Energy Use

The total energy consumed by the agricultural sector in 1997, the date of the last Agricultural Census, is shown in Table 2-5. Energy use includes inputs to both crop and animal farming operations. Agriculture has become more energy efficient over the last two decades through adoption of conservation tillage practices, switching to more fuel-efficient diesel engines, and improved methods of crop drying and irrigation. Conservation tillage uses less energy as it requires less field preparation prior to planting. As farm size has grown, producers have moved toward more energy-efficient, diesel-powered tractors and self-propelled equipment. Gasoline use has dropped considerably since 1965 (by over 30%) as a result of the switch to diesel. Use of agricultural chemicals, which accounts for direct and indirect energy use, increased considerably during the 1980s, but has remained relatively stable over the last decade [USDA 2000d].

Table 2-5. Direct Use of Fuel and Electricity In Agriculture, 2000

Fuel Type	Physical Units	Trillion Btu	% of Use
Gasoline and Gasohol (M gal)	1,710	214	20
Diesel Fuel (M gal)	2,445	339	31
Natural Gas (bcf)	75	77	7
Other Fuels* (M gal)	1,602	221	21
Electricity (b kWh)**	65	221	21
TOTAL		1,072	100%

*LP gas, fuel oil, kerosene, motor oil, grease

**Estimated as a percentage of farm expenditures, priced at 4 cents/kWh

Data for farm use of electricity has not been collected since 1991 – electricity is estimated based on historical use. Data does not include personal farm use of fuels and electricity.

Source: USDA 2000b, EIA AER 2001, USDA NASS 1997

The cost of energy can have a substantial impact on crop producers. The dramatic increases in natural gas prices experienced in 2001, for example, increased farm costs for irrigation and grain drying. Since natural gas is a primary feedstock for anhydrous ammonia, the main ingredient in nitrogen fertilizers, these costs are passed along to producers when natural gas prices increase. In periods of dramatic price hikes, fertilizer producers may stop or severely reduce production, forcing farmers to rely on more expensive imports. To compensate, farmers may also reduce production of nitrogen-intensive crops such as corn [USDA 2001].

Volatility in energy prices and the subsequent ripple effects could impact the cost-competitiveness of bioproducts. Farming methods that minimize the effects of energy volatility will be key to creating a sustainable feedstock infrastructure.

Energy Used in Crop Production

Energy expenditures in crop production depend on the agricultural practices employed. Crops that require drying or irrigation, for example, have much higher fuel intensity ratios. Crops that require high-volume nitrogen applications (such as corn) will exhibit higher combined direct and indirect energy use per acre than those that require less nitrogen. Soil and weather conditions impact irrigation and fertilizer application as well.

Fuels used in farm equipment for tilling, planting, irrigation, harvesting and other activities comprise the largest use of energy in crop production. Other major components in the energy equation are the rates of application of fertilizers and agricultural chemicals.

The energy associated with the manufacture and application of fertilizers, pesticides and herbicides can be a significant factor. Not only is energy required to apply these chemicals, but considerable energy is used during their manufacture in the chemicals industry. Although the farmer does not directly consume this manufacturing energy, it is still an important element in the life cycle costs associated with crop production. Table 2-6 provides some average energy use for the manufacture of agricultural chemicals.

Energy used for pumping water in irrigation systems can also be significant, and varies considerably depending upon the type of irrigation system used and fuel input. Electricity and natural gas systems require the most energy, while diesel or gasoline-driven systems require the least energy. The fuel expended for irrigation for all crops in 1994 is shown in Table 2-7 [USDA 1994].

Table 2-6 Energy Used to Produce Agricultural Chemicals (Btu/lb)

Chemical	Diesel	Natural Gas	Electricity
Nitrogen	0	16,857	321
Phosphoric Acid	0	56	734
Potash	642	559	870
Herbicides	67,310	25,802	19,107
Insecticides	69,299	26,564	19,790

Source: USDA 2002

Table 2-7 Energy Used in Crop Irrigation, 1994

Energy Input	T Btu/Yr	Million Btu/Acre	$/acre
Electricity	58.3	3.0	41.45
Natural Gas	63.8	10.5	31.21
LPG, Propane	9.2	5.7	17.00
Diesel	19.0	2.3	20.35
Gasoline/ Gasohol	0.4	2.3	20.23

Source: USDA 1994

The relative use of fuels, agricultural chemicals, fertilizers and other energy inputs is illustrated in Tables 2-8 and 2-9 for the production of corn and soybeans, respectively. The data represents average national values and does not reflect variances due to best practices or the use of state-of-the-art technology. A state-of-the-art farming operation, for example, might use from 10-40% less energy overall [ILSR 1995].

Considerable disparity exists in the data available on energy inputs to production of individual crops in the U.S. A recent study by the USDA of nine different reports on energy inputs to corn production found as much as a 40% variation in energy use data [USDA 2002]. The variations are due to different assumptions about crop yields and farm practices, use of older data (which tends to overestimate energy use), and use of lower versus higher heating values.

Table 2-8 Estimated Energy Inputs to Corn Production

Input	Btu/Bushel	Btu/Acre
Seed	242	30,250
Fertilizer (Total)	21,737	2,717,125
Nitrogen	19,082	2,385,250
Phosphate	789	98,625
Potash	1,776	222,000
Lime	90	11,250
Fuel (Total)	22,002	2,750,250
Diesel	11,175	1,396,875
Gasoline	3,859	482,375
LP Gas	5,200	650,000
Natural Gas	1,768	221,000
Electricity	5,665	708,125
Pesticides and Herbicides	3,797	474,625
Other*	4,029	503,625
TOTAL	57,476	7,184,500

*Includes hauling, custom work

Source: USDA 2002 (yield of 125 bushels/acre, weighted average for nine corn-producing states)

Table 2-9 Estimated Energy Inputs to Soybean Production

Input	Btu/Bushel	Btu/Acre
Seed	na	na
Fertilizer (Total)	6,259	237,843
Nitrogen	2,660	101,086
Phosphate	1,516	57,618
Potash	2,083	79,139
Fuel	20,446	776,940
Pesticides and Herbicides	5,254	199,663
Other*	9,403	357,299
TOTAL	41,362	1,571,745

na not available

Source: ILSR 1994a (yield of 38 bushels/acre, national average)

*Includes lime, hauling, custom work

A comparison of energy inputs for the major crops is shown in Table 2-10. These have been estimated based on current crop yields, values in Table 2.6, and published energy use data. Energy use for fertilizers, pesticides and herbicides represents energy used in the manufacturing of these chemicals. Fuels used in the application of chemicals are included in mechanized operations.

Optimizing agricultural practices to minimize energy use could be a key component of the future biomass feedstock infrastructure. On the farm, mechanized operations (tilling, planting,

Table 2-10 Major Energy Inputs for Selected Crops (Btu/bushel)

Operation	Corn	Soybeans	Wheat	Rice	Barley
Mechanized Operations	22,002	20,446	40,500	32,400	24,000
Fertilizer	21,737	6,259	23,892	28,800	16,080
Pesticides & Herbicides	3,797	5,254	800	5,580	11,000
Irrigation	na	na	na	33,750	na
Other	4,029	9,403	na	na	na

Shading indicates data from older source.
na not yet available; under construction.
Sources: USDA 2002, USDA-NASS 2001, ILSR 1994, ILSR 1995, ORAU 1985.

harvesting) account for the largest share of energy use. When looking at the life cycle costs of biomass as a feedstock, fertilizers and agricultural chemicals represent significant energy consumption and costs that are passed on to the farmer. Minimizing the use of fertilizers, chemicals and energy-intensive farm practices could help to reduce production costs and ultimately the cost-competitiveness of biomass with petroleum.

2.4 Environmental Issues and Feedstock Sustainability

Sustainability -- environmental soundness, stewardship of resources, and preserving a viable society for future generations -- is an important consideration for the future of bioenergy.

Methods such as conservation tilling, advanced agricultural systems, improved irrigation and water management will all contribute to sustainability. The use of GM crops and trees offer great promise to reduce the use of fertilizers and pesticides, and to even produce plants that are resistant to drought and other climatic conditions.

The impacts of agriculture on air, land and water are issues that must be considered in the sustainable production of biomass for feedstocks. When compared with the production of oil and gas, and the refining of petroleum into feedstocks, these impacts may seem relatively small. However, understanding the environmental impacts of crop production is important to creating sustainable and cost-competitive bioproducts.

Emissions to the Air

Agricultural activities produce emissions of particulate matter (PM), nitrogen and sulfur compounds, and volatile organic compounds (VOCs). These emissions result primarily from the application of fertilizers, pesticides and herbicides.

The application of fertilizers (gaseous, liquid, or solid) can produce emissions immediately during or shortly after the application, as well as latent emissions (days or weeks later). The source of these emissions is sometimes a reaction of the soil with the fertilizer, which produces nitrogen compounds such as NO, N_2O, NH_3, and SO_2. The fertilizer can also volatilize immediately, releasing NH_3 and fertilizer compound. Soil disturbances such as tilling or wind erosion can create PM emissions that become airborne. In some cases, the solid fertilizer can volatilize above the fertilizer trailer, generating gaseous NH_3 as well as fertilizer.

Some heavy metals have been identified in soils treated with phosphate, nitrogen, and manure fertilizers, and could become airborne along with fugitive dust emissions. While some of these elements occur naturally, others can be attributed to fertilizer application.

Those identified in soil and listed as Hazardous Air Pollutants (HAPs) include cadmium, mercury, nickel, selenium, chromium, manganese, lead, cobalt. The contribution of agriculture to the emissions of particulates containing these heavy metals is still uncertain.

The application of pesticides and herbicides releases organic compounds and particulates. Most of the active ingredients in synthetic pesticides have some degree of volatility, but are not considered to be highly volatile, except for fumigants. Over time, a portion of the active ingredients will volatilize into the atmosphere. Fumigant active ingredients may volatilize immediately. Inert ingredients are major contributors to emissions that occur within 30 days [EPA 2001a].

A great deal of study has been devoted to the environmental and safety issues connected with the application of chemicals in agriculture and forests. Many contain volatile organic compounds (VOCs) that volatilize over time and contribute to air pollution. The application of these chemicals in dry form also contributes to the emission of particulate matter to the atmosphere.

Pesticides also pose a risk to the aquatic environment as they may enter surface waters, potentially contaminating ground and drinking water supplies. Particulate matter emissions from adsorbed active ingredients in pesticides can occur during the application of dusts used as pesticide carriers or during wind erosion [EPA 1995].

Mitigation of air pollutants from agriculture is important for all crop production, regardless of whether it is used for food, feed, or bioenergy. Where bioproducts are concerned, practices that reduce the need for agricultural chemicals and fertilizers while retaining crop yields and quality would contribute to sustainability and increase the viability of biomass as a feedstock resource.

Impacts on Water

Only about 50% of the nitrogen applied as fertilizer is taken up by plants; the remainder washes off or is blown off the soil. Run-off of nitrogen and phosphate from fertilizers results in eutrophication of surface waters such as lakes, streams and rivers. Eutrophication is a natural process where a water body is enriched by the addition of excessive nutrients, which causes excessive algae growth and depletes oxygen. Many species cannot survive in these conditions, and large “dead zones” appear from decaying matter undergoing anaerobic degradation. Eutrophication is creating huge dead zones in some parts of the U.S. (e.g., Mississippi delta) [UCD 2002, EPA 2002c].

Water pollution occurs from the use of some toxic herbicides and pesticides and in some cases from fertilizers. These chemicals can enter surface waters by direct application, drift, mobilization in ephemeral streams, over-land flows, and leaching. Direct application or spills are the primary source.

The health risk of these compounds depends on the pesticide toxicity and amount of pesticide exposure. The only known carcinogen found in pesticides is arsenic, and use of this compound has declined substantially. Nitrates pose health threats, particularly to infants, as they can prevent oxygen transport. Excessive phosphates can also degrade water quality. [UCD 2002, EPA 2002b, EPA 2002c, ISU 1995].

Soil Carbon Depletion

Soil carbon depletion is another consideration in the future production infrastructure for biomass feedstocks. Production of dedicated feedstock crops should incorporate sustainable agricultural practices that minimize the depletion of carbon from the soil.

The capacity for the storage of carbon in soil is tremendous. However, carbon is depleted from the soil continually, in part from human activities. It has been estimated that about 100 billion tons of carbon originally in the Earth's soil has been lost through human activity, primarily agriculture [Wojick 1999].

Organic carbon makes the soil fertile for growing. Depletion is caused in large part by soil erosion (wind and water) and ineffectual crop planting practices. Numerous practices are undertaken to increase the carbon storage in soil, such as restoration of degraded soils (improved crop rotation practices), erosion control through conservation tillage, soil fertility management, supplemental irrigation, and improved cropping systems and winter cover. Figure 2-4 illustrates the dramatic changes in soil carbon with tilling methods in corn production over the last 90 years.

The increased sequestration of carbon in the soil from improved agricultural practices could have significant impacts for global warming. It has been estimated that carbon sequestration in cultivated soils could potentially range from as much as 50-70 million metric tons of carbon equivalents per year over a 25-50 year period [Johnston 1999].

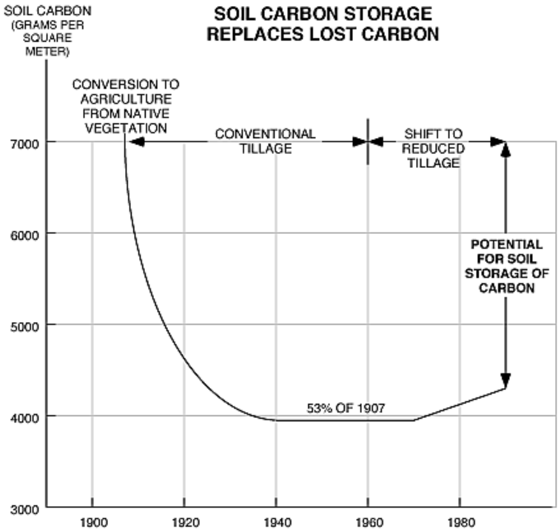


Figure 2-4 Simulated Total Soil Carbon Chanages (2-20 cm depth) From 1907 to 1999 for the Central Corn Belt [Wojick 1999]

3.0 Opportunities for Industrial Bioproducts

3.1 Summary of Potential Industrial Bioproduct Opportunities

The U.S. has abundant biomass resources and with the right technology, has the potential to convert these renewable resources into valuable industrial products and bioenergy. The success of new bioproducts will largely depend on whether they can be produced economically as well as their performance in targeted applications.

Potential markets for bioproducts are wide-ranging, and include polymers, lubricants, solvents, adhesives, herbicides, and pharmaceuticals. While bioproducts have already penetrated most of these markets to some degree, new products and technologies are emerging with the potential to further enhance performance, cost-competitiveness, and market share. The primary markets for bioproducts are shown in Table 3-1.

Organic chemicals represent the most direct and largest target for bioproducts. What makes a chemical organic is that it is primarily composed of carbon and hydrogen—the same primary constituents of biomass. Using novel chemistries, the carbons present in biomass (carbohydrates) can be rearranged to yield products that are the equivalent of or superior to the products that are now produced from fossil energy (hydrocarbons).

Many of the commodity organic chemicals serve as monomers for **plastics** (polymers), which represent a tremendous opportunity for bioproducts with an annual production of over 100 billion pounds. Almost all of the polymers produced today are petroleum-based, with the only major exceptions being cellulose polymers and natural rubber.

Advances in biotechnology, chemicals processing, chemistry and separations are opening up new avenues for biobased polymers such as polylactide (now in production) and polytrimethylene terephthalate (soon to be partially biobased).

Other major organic chemicals markets for bioproducts include **organic acids, alcohols, and solvents.** Biomass-based ethanol (used mostly for fuels, but some industrial uses) is an established industry. There are emerging markets for other alcohols and bio-derived acids.

Table 3-1 Annual Domestic Organic Chemical Production

Market	Production (Billion lb)
Lubricants and Greases (2001)	**19.6**
All Organic Chemicals[1]	**175.2**
Polymers[2] (2001)	101.1
Polyolefins (HDPE, LLDPE, LDPE, PP)	*49.2*
PET	*6.9*
Polyvinyl Chloride	*14.3*
Styrenics	*9.0*
Nylon	*1.1*
Thermosets	*8.0*
Other Polymers	*12.6*
Forest Chemicals[3] (1999 and 2000)	2.8
Solvents (2001)	10.6
Glycols (2000)	*3.0*
Other Organic Chemicals (1997)	60.7
TOTAL	**194.8**

[1] Estimates represent the net volume of organic chemicals produced in the United States and they do not double count volumes of intermediates and their derivatives.
[2] Data from *APC Year-End Statistics for 2002, Production, Sales & Captive Use, 2002 vs. 2001,* American Plastics Council's Plastic Industry Producers' Statistics Group, as compiled by VERIS Consulting, LLC; APC.
[3] Tall oil, gum rosin, and crude sulfate turpentine.

Sources: DOC-ASM 1999, APC 2002, FG 2001, EIA 2001, CMR 2001j, CMR 2001k, CMR 2001l, CMR 1998c, CMR 2000d, CMR 2000e

While **lubricants and greases** are now mostly petroleum-based, they were originally plant-based because they could be made from vegetable oils with little modification. With energy prices on the rise, and growing environmental concerns over the impacts of petroleum-based products, vegetable oil-based lubricants and greases are making an entrance back in the market. With new chemistries and processes making them more economical, they could regain significant market share.

The potential opportunities for new bioproducts, are summarized in Table 3-2. These are categorized according to the technology platform used to convert the biomass feedstock (e.g., fermentation, gasification). The connection between biomass composition, conversion platforms and potential products, as well as the details behind the key opportunities, are outlined in the following sections.

Table 3-2 Summary of Industrial Biobased Product Opportunities

Technology Platform	Chemical	Applications	Current U.S. Market Size (million lb)	Potential 2020 Biobased Market Size (million lb)
Sugars Fermentation	Lactic Acid (currently biobased)	Acidulant (food, drink), electroplating bath additive, mordant, textile/leather auxiliary	<5 (industrial uses)	Expect GDP-like growth
	Polylactide (currently biobased)	Film and thermoformed packaging, fiber and fiberfill applications	Packaging: 21,289 Fiber/fiberfill: 2,769	8,000
	Ethyl Lactate (currently biobased)	Solvent (blending with methyl soyate), chemical intermediate	8,000-10,000	>1,000
	1,3-Propanediol	Apparel, upholstery, specialty resins, and other applications	Small	500
	Succinic Acid	Surfactants/detergents, ion chelator (electroplating), food, pharmaceuticals, antibiotics, amino acids, and vitamin production	US: small World: 33	GDP-like growth
	Succinic Acid Derivatives (tetrahydro-furan, 1,4-butanediol, γ-butyrolactone, N-methyl pyrrolidone, 2-pyrrolidone, succinate salts)	Solvents, adhesives, printing inks, magnetic tapes, coating resins, plasticizer/emulsifier, deicing compounds, herbicide ingredient, chemical and pharmaceutical intermediates	1,395	>90
	Bionolle 4,4 polyester	Thermoplastic polymer applications	25,000-60,000	>4,000

Table 3-2 Summary of Industrial Biobased Product Opportunities

Technology Platform	Chemical	Applications	Current U.S. Market Size (million lb)	Potential 2020 Biobased Market Size (million lb)
	3-Hydroxypropionic Acid & Derivatives (acrylic acid, acrylonitrile, acrylamide, 1,3-propanediol)	Acrylates, acrylic fibers, polymers, resins	5,336	Technology now just being developed
	N-Butanol	Solvent, plasticizer, polymers, resins	1,850	Could be significant
	Itaconic Acid	Current: aluminum anodizing reagent, reactive comonomer Potential: methyl methacrylate applications, acrylic pressure sensitive adhesives	1,808 (itaconic acid and its derivatives)	Significant if technology is successful
Sugars Fermentation & Thermochemical	Propylene Glycol	Solvents, heat-transfer fluids, humectants, plasticizers, polyurethane chain extenders, antifreeze	1,100	>500
Sugars Thermochemical	Isosorbide (currently biobased)	Current: active ingredient in diuretic and antianginal drugs Potential: polymer additive	Small	If technology is successful, could be 100-300
	Levulinic Acid & Derivatives (methyl tetrahydrofuran, δ-amino levulinic acid, diphenolic acid, tetrahydrofuran, 1,4-butanediol)	Oxygenates for fuels, biodegradable herbicide, bisphenol A alternative, comonomer, solvent	Oxygenate: 30,800 Others: 2,845	Oxygenate: not projected (challenging to penetrate this market) Others: 300-500
Oils & Lipids	Lubricants & Hydraulic Fluids	Lubricants and Hydraulic Fluids	20,000	Significant
	Solvents	Solvents	8,000-10,000	Significant
	Polymers (Polyurethanes are most significant)	Polyurethanes	5,327	Significant
	Proteins	Unknown	Unknown	Unknown
Biomass Gasification	Fischer-Tropsch & Gas-to-Liquids Products	Fuels (transportation, heating), solvent, aerosols, oxygenate, chemical intermediates	Very large markets	Will require more favorable economics
Biomass Pyrolysis	Phenol-Formaldehyde Resins	Plywood, oriented strand board (OSB), and other wood composites	3,900	Significant
Biocomposites	Biocomposites	Unknown	Unknown	Unknown
Plants as Factories	Guayule	Natural rubber applications	2,184	Not projected
	Polyhydroxy-alkanoates (PHAs)	Thermoplastic polymer applications	30,000	If technology is successful, could be >4,000
Photosynthesis, Anaerobic Digestion	Lignin, methane, carbon dioxide, other chemicals	Unknown	Unknown	Unknown

3.2 The Composition of Biomass

The composition of the biomass feedstock determines the ease with which the biomass can be converted to useful products or intermediates, and influences the functionality of the final product. Biomass contains a variety of components, some of which are readily accessible and others that are much more difficult and costly to extract. The composition and subsequent conversion issues for current and potential biomass feedstock components are outlined in the following sections.

Starch (Glucose)

Starch, which is essentially glucose, is readily recovered and converted from grains (corn, wheat, rice) into products. Starch from corn grain provides the primary feedstock for today's existing and emerging sugar-based bioproducts, such as polylactide as well as the entire fuel ethanol industry.

Starch is composed of glucose, but it is a mixture of α-amylose and amylopectin (see Figures 3-1 and 3-2). 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 [Garrett 1995]. 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.

Corn grain serves as the primary feedstock for starch used to manufacture today's biobased products. Corn wet mills use a multi-step process to separate starch from the germ, gluten (protein), and fiber components of corn grain. The starch streams generated by wet milling are highly pure, and acid or enzymatic hydrolysis is used to break the α-1,6-glycosidic linkages of starch to yield glucose. Glucose is then converted into a multitude of useful products (see Figure 1-1 and Appendix A).

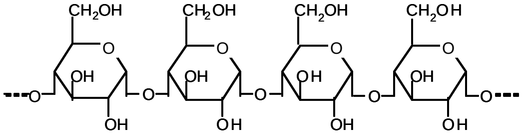


Figure 3-1 Alpha-Amylose Structure
[Garrett 1995]

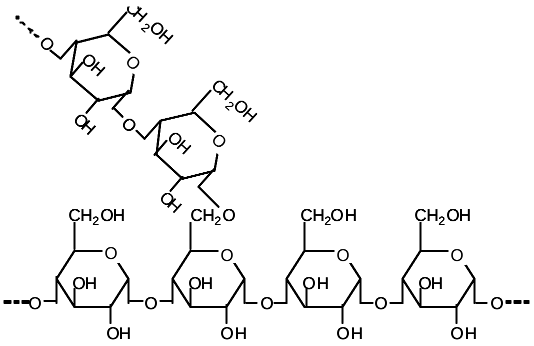


Figure 3-2 Amylopectin Structures
[Garrett 1995]

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 also contain valuable components, but they are not as readily accessible as starch. These **lignocellulosic** biomass resources (also called cellulosic) are comprised of cellulose, hemicellulose, and lignin. 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 perceived as a valuable and largely untapped resource for the future bioindustry. However, recovering the components in a cost-effective way represents a significant technical challenge.

Cellulose

Cellulose is one of nature's polymers and is composed of glucose, a six-carbon sugar. The glucose molecules are joined by β-1,4-glycosidic linkages which allow the glucose chains to assume an extended ribbon conformation (see Figure 3-3). Hydrogen bonding between chains leads to the formation of flat sheets that lay on top of one another in a staggered fashion, similar to the way staggered bricks add strength and stability to a wall. As a result, cellulose is very chemically stable and insoluble and serves as a structural component in plant walls.

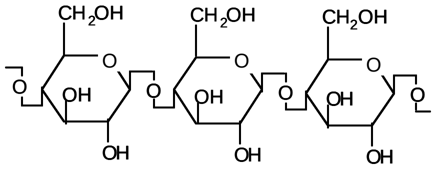


Figure 3-3 Partial Structure of Cellulose [Lee 1996]

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. Harnessing the sugars of lignocellulosics therefore involves a pretreatment stage to reduce the recalcitrance (resistance) of the biomass to cellulose hydrolysis.

The effectiveness of the pretreatment stage is key to successful conversion to sugars. Thermal and chemical pretreatment methods include autohydrolysis, steam explosion, acid prehydrolysis, organosolv pretreatment, and others. Arkenol, Inc. has developed a concentrated acid process that pretreats and hydrolyzes the cellulose to fermentable sugars [Arkenol 1999]. The goal of these processes is to solubilize the hemicellulose and in some cases, a portion of the lignin, in order to "unlock' the cellulose-hemicellulose-lignin matrix. The pretreatment "exposes" the cellulose and makes it more susceptible to acid or enzymatic hydrolysis, the process which breaks down cellulose into glucose (saccharification).

An alternative pretreatment method is the use of cellulase enzymes to break cellulose down into glucose, following a suitable pre-treatment step. The major barrier to the use of cellulase enzymes is cost and several DOE-funded efforts are underway to reduce the economics of cellulase production and use. Technical barriers include enzyme inhibition by glucose (referred to as product inhibition) and deactivation of the enzymes by lignin that has not been removed during pretreatment.

The most important improvement to enzymatic cellulose hydrolysis has been the development of simultaneous saccharification and fermentation (SSF). SSF significantly reduces the effects of glucose inhibition of the cellulase enzymes, enabling a more effective process. However, SSF can only be used when the sugars are to be fermented to the chemical intermediate. More advances in cellulose hydrolysis technologies are necessary for the cost effective production of sugars for lignocellulosic biomass.

In the past, technologies to process cellulosic materials to glucose were considered a low priority next to starch recovery due to the recalcitrance of cellulose. With advances in technology, researchers have begun exploring agricultural residues and energy crops as an abundant renewable source of cellulose. The ability to cost-effectively tap this potentially large resource could facilitate the introduction of new bioproducts.

Hemicellulose

Hemicellulose is a polymer containing primarily 5-carbon sugars such as xylose and arabinose (see Figures 3-4 and 3-5) with some glucose and mannose dispersed throughout. It forms a short-chain polymer that interacts with cellulose and lignin to form a matrix in the plant wall, 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

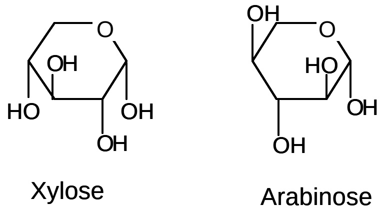


Figure 3-4 Structure of 5-Carbon Sugars in Hemicellulose

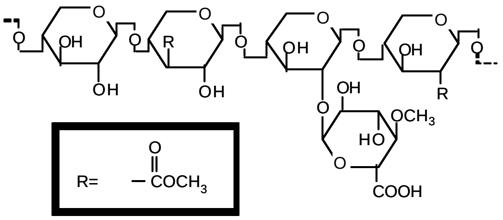


Figure 3-5 General Structure of Hemicellulose [Lee 1996]

during the pretreatment stage. Some of the hemicellulose is too intertwined with the lignin and is unrecoverable.

Pretreatment conditions must be optimized to prevent pentose and hexose sugars from being degraded to products that can inhibit downstream processing. Pretreatment under less severe conditions can reduce the amount of sugar degradation while still achieving a high degree of hemicellulose hydrolysis.

Similar to cellulose enzymes, hemicellulase enzymes can be used to recover a significant fraction of the hemicellulose from lignocellulosic material. The enzymatic hydrolysis of hemicellulose is much easier than that of cellulose and is already being used industrially by the pulp and paper industry. Hemicellulase enzymes are used to modify the wood fibers and improve pulp bleachability.

DOE is funding research on the recovery of residual starch and hemicellulose from corn fiber using a combination of acid hydrolysis and enzymatic hydrolysis. Mild acid hydrolysis coupled with the use of α-amylase, amyloglucosidase, and hemicellulases has been shown to yield a high conversion of starch and hemicellulose to hexose and pentose sugars.

Lignin

Lignin helps bind the cellulose/hemicellulose matrix while adding flexibility to the mix. 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) (see Figure 3-6). The ring structures of lignin have great potential as valuable chemical intermediates. 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 a high-phenolic content oil which is used as a partial replacement for phenol in phenol-formaldehyde resins. New chemistries and separations technology that can fractionate lignin into its discrete substances for further processing could create opportunities for lignin as a feedstock for bioproducts.

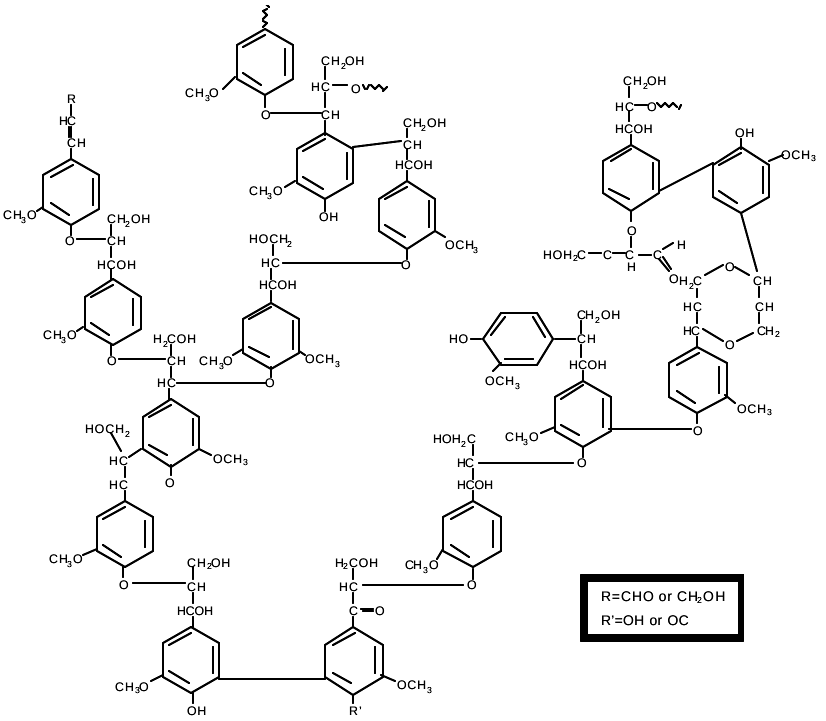


Figure 3-6 Partial Structure of Lignin [Lee 1996]

Oils and Protein

The seeds of certain plants offer two families of compounds with great potential for bioproducts: oils and protein. Oils and protein are found in the seeds of certain plants (soybeans, castor beans), and can be extracted in a variety of ways. Plants raised for this purpose include soy, corn, sunflower, safflower, rapeseed, and others. A large portion of the oil and protein recovered from oilseeds and corn is processed for human or animal consumption, but they can also serve as raw materials for lubricants, hydraulic fluids, polymers, and a host of other products.

Vegetable Oils

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 3-7. In this example, the three fatty acids are all lauric acid, but could be a mixture of two or more.

Fatty acids differ in their chain length as well as the degree of unsaturation (see Figure 3-8). 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. Typical compositions for oils from oilseeds are given in Table 3-3.

Fatty Acid Naming Convention

Oleic acid C18:1 Δ^9.

18 carbons, one unsaturated bond on the ninth carbon

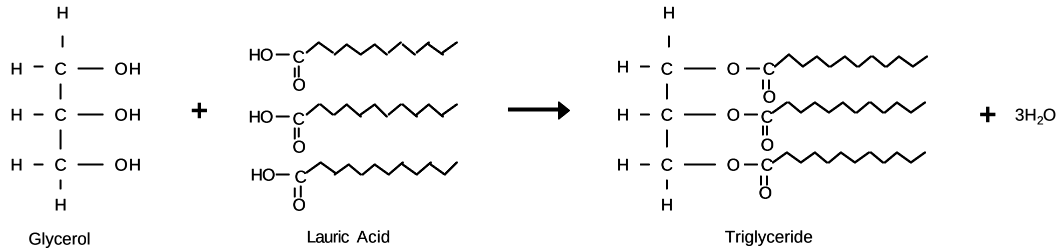


Figure 3-7 Synthesis of a Triglyceride

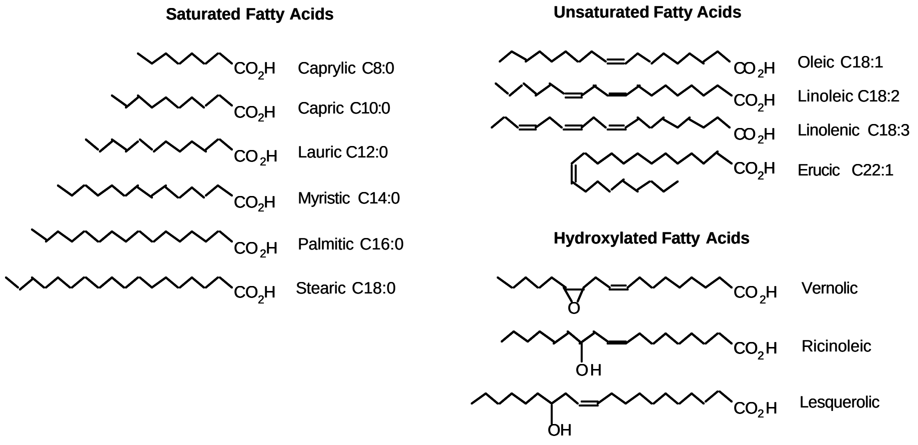


Figure 3-8 Structures of Fatty Acids Common in Vegetable Oils

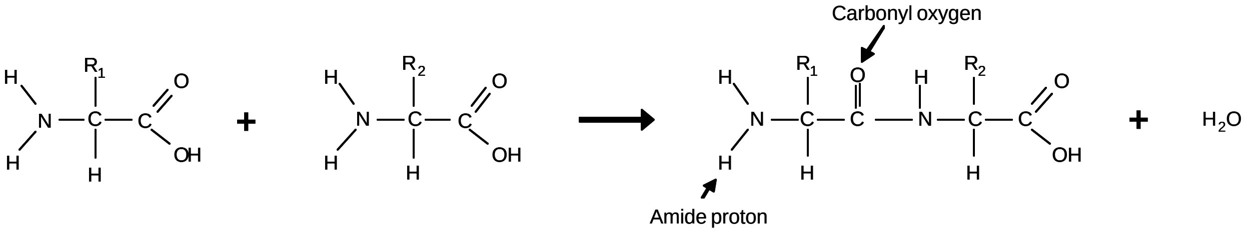


Figure 3-9 Synthesis of a Polypeptide (Protein)

Proteins

Proteins are natural polymers with amino acids as the monomer unit. They are incredibly complex materials and their functional properties depend on molecular structure. There are 20 amino acids each differentiated by their side chain or R-group and they can be classified as nonpolar and hydrophobic, polar uncharged, and ionizable. The interactions among the side chains, the amide protons, and the carbonyl oxygens help create the protein's 3-D shape.

A protein can consist of a single polypeptide (amino acid polymer) or two or more polypeptide chains (see Figure 3-9). The protein structure determines its properties and this structure begins with the amino acid sequence, sometimes referred to as the primary structure.

The chemical properties of a protein can be altered by modifying the amino acid sequence. A substitution of one or more amino acids for others can change the interactions that occur between individual amino acids within a polypeptide, and alter the way the chain coils (secondary structure) and the way the coil folds (tertiary structure). In proteins containing multiple polypeptides, the manner in which the polypeptide chains interact (quaternary structure) can also be altered.

Proteins have very unique crystalline structures that can provide unmatched performance as materials. Spider silk, for example, has fiber strength and elasticity properties that no synthetic fiber comes close to. Certain aquatic organisms produce proteins with unmatched tenacious adhesive properties. Utilizing and modifying natural proteins for novel materials holds tremendous promise, but is an area that has barely been explored.

Table 3-3 Oilseed Composition and Fatty Acid Profiles

Oilseed	Oilseed Composition			Fatty Acid Profile of Oil							
	Fiber (%)	Protein (%)	Oil (%)	Fatty acid 1	%	Fatty acid 2	%	Fatty acid 3	%	Fatty acid 4	%
Soybean	5	>35	17-21	Linoleic	51-56	Oleic	23	Palmitic	12	Linolenic	6
				Oleic	53	Linoleic	32	Palmitic	9	Stearic	3
				Linoleic	54	Oleic	34	Palmitic	4	& linolenic	4
Corn	2-4	8-14	3-6	Linoleic	54-60	Oleic	25-31	Palmitic	11-13	Stearic	2-3
Canola		40-46	43-47	Oleic	64	Linoleic	22	Linolenic	8	Palmitic	3
Rapeseed				Erucic	>40	Linoleic	22	Oleic	19	Linolenic	8
Coconut		21.2	65-68	Lauric	49						
Cottonseed	23	19	15-24	Linoleic	50	Linolenic	<1				
Palm Kernel	6-7	17-19	49	Lauric	48	Myristic	16	Oleic	15		
Palm				Palmitic	42-44	Oleic	40	Stearic	5		
Sunflower (high linoleic)	13-16	16-20	40-50	Linoleic	32-75	Oleic	21	Linolenic	<1		
Sunflower (high oleic)	13-16	16-20	40-50	Oleic	>80	Linoleic	<10	Linolenic	<1		
Safflower		20-22	25-40	Linoleic	73-80	Linolenic	15				
Safflower (high oleic)		20-22	25-40	Oleic	78	Linoleic	12				
Castor	25-35	17-25	46-52	Ricinoleic	90	Linoleic	3				
Crambe		24	40-46	Erucic	55-60						
Linseed		24	35-44								
Meadowfoam		16-25	18-33	>C20	98						
Jojoba[1]			41-57	>C20	94						
Vermonia galamensis			35-42	Vernolic	72-78						
Stokes aster			30-40								
Cuphea			30-36	Capric	<91	Lauric	*	Myristic	*	Caprylic	*
Lesquerella			17-29	Lesquerolic	46-82						

* indicates no information is available

Sources: Rossell 1991, SCRI 2002, NPP 1999, PNG 1996a, CRA 1996, USB 2002

3.3 Emerging and Developing Industrial Bioproducts

Today in the U.S., over 12 billion pounds of industrial bioproducts (excluding conventional lumber pulp and paper) are produced from domestic biomass (see Table 3-4). Starch and sugars and products from the forest products industry comprise the largest share of today's bioproducts.

Oils and lipids are used in a wide variety of products, from personal care to printing inks. A fair amount of biomass components, primarily oils and fatty acids, are imported for refining and use in many applications, the largest being surfactants and detergents.

New bioproducts are continuously emerging, and the opportunities to use biomass in novel products are just beginning to be explored. In the following sections, key emerging and potential bioproducts are discussed according to the feedstock and technology platforms (biochemical, thermochemical) by which they are produced.

Table 3-4 Current Industrial Bioproduct Production from Domestic Biomass

Category	Principal Technologies	Feedstock	Chemical	General Product	Annual Biobased Production (M lb)
Starch and Sugars[1]	Biochemical	Biomass sugars derived from corn and sorghum	Lactic acid, citric acid, ethanol, starch, sorbitol, levulinic acid, itaconic acid	Polymers, solvents, cleaners, coatings, inks, detergents/surfactants, pharmaceuticals, adhesives, paints, composites, laminates, toiletries, cosmetics	5,413
Oil/Lipids	Thermochemical	Oils/lipids derived from soybean, rapeseed (high erucic acid rapeseed)	Glycerol/glycerine, alkyd resins, high erucic acid rapeseed, polyurethane, epoxidized soybean oil, factice, sulfurized fatty oils, fatty acids, cyclo-pentadienized oils, lecithin, maleinized oils	Pharmaceuticals, personal care, urethanes, alkyd resins, plasticizers, lubricants, paints, resins, printing inks, industrial and textile finishes, semi-rigid foam, thermoplastic elastomers, cosmetics, coatings, surfactants, sealants, caulks, pesticides	1,589
Specialty Crops	Thermochemical	Spearmint, peppermint, sweet almond	Spearmint oil, peppermint oil, sweet almond oil	Personal care, pharmaceuticals, epoxy and alkyd resins, paints, cosmetics, and toiletries	9
Forest Derivatives	Thermochemical	Pine, black liquor, and soft wood	Turpentine oil, rosin, tall oil, and cellulose derivatives (esters, acetates, etc.)	Solvents, soaps, detergents, toiletries, perfumes, rubber, adhesives, coatings, printing inks, phenolic resins, plastics, textiles	5,326
Total					12,337

[1] The ethanol and citric acid included here are for industrial use only (e.g., solvent, cleaning reagent).

Sources: Ashford 2001, CMR 2001d, Biocycle 2001, CHEM EXPO 2001, CMR 2001g, CHEM EXPO 2000, RE 1998, FG 2000, CMR 2001h, PE 2000, PRN 2000, CMR 1999b, WA 1999, CSR 1999, CMR 1998, CMR 2000, SCCS 1998, CMR 1997, Purchasing 2000, CW 2000, USB 2001, CMR 1999c, CMR 2001i, CMR 1998b, CMR 2000a, CMR 2000b, CMR 2000C, CMR 2001j, CW 1998, CMR 2000d, ACC 2000, CEH 2002, CW 2000a, CMR 1996, AT 2000, CW 1999

Biomass Conversion Technology Platforms

There are many processes for converting biomass components to value-added products, fuels, and power. They can be broadly classified as biochemical or thermochemical.

Biochemical technologies use enzymes or microorganisms to convert the feedstock to the desired product (e.g., fermentation) or the product is produced within the plant (e.g., extractives, fiber). Fermentation processes are most commonly used for the production of organic acids and ethanol. Plants that produce bioproducts within their tissues are sometimes referred to as "plants as factories." Common examples include paper and cotton fiber.

Thermochemical technologies utilize catalysts (acid, metal, or a combination) and/or high pressure and temperature to convert biomass components to the desired product. Oils and bioproducts from woody resources are typically processed using thermochemical methods. Thermochemical processes such as gasification and pyrolysis have been explored to some degree for the production of bioproducts but are not in widespread commercial use.

In some cases, products can be derived from more than one conversion technology, or can be produced in a series of steps that involve both thermochemical and biochemical processes (e.g., sugars). Table 3-5 lists the primary technology platforms for the manufacture of bioproducts, and the overlaps between platforms and conversion methods.

The specific bioproducts that can be produced via each of these technology platforms, and the current technical challenges and markets for each are outlined in the following sections.

Table 3-5 Technology Platforms and Type of Conversion

Platform	Primary Type of Conversion	Overlaps
Sugars Fermentation	Biochemical	Further processing can be thermochemical
Sugars Thermochemical	Thermochemical	
Oils/Lipids	Thermochemical	
Protein	Thermochemical	
Gasification	Thermochemical	
Pyrolysis	Thermochemical	
Lignin	Not Developed	To date, the pyrolysis of lignin has been explored
Biocomposites	Thermochemical	Composites utilizing materials such as plant fiber also fall under plants as factories
Plants as Factories [*Note: The desired molecule is present in the biomass and only requires extraction and minimal processing]*	Biochemical	Processing of extracted compounds can be thermochemical
Photosynthetic Organisms	Biochemical	
Anaerobic Digestion	Biochemical	Produces methane which can be upgraded thermochemically

3.3.1 Fermentation of C6 Sugars (Glucose) to Bioproducts

Biomass sugars represent the most abundant renewable resource available. While there are many ways to transform sugars into bioproducts, many of the products we are familiar with today (citric acid, ethanol, lactic acid) are produced through fermentation. With the vast range of microorganisms available and many being newly discovered and exploited, the fermentation of sugars holds great potential for new bioproducts.

Two types of sugars are present in biomass: 6-carbon sugars or hexoses, of which glucose is the most common, and 5-carbon sugars or pentoses, of which xylose is most common. Glucose derivatives are the most promising, and include lactic acid, succinic acid, butanol, 3-hydroxypropionic acid, 1,3-propanediol polyhydroxyalkanoates (PHAs), and L-lysine.

Lactic Acid Fermentation Platform

Lactic acid is commercially produced today through the fermentation of glucose. Approximately 72 million pounds are used annually in the U.S., primarily in food and beverages. Lactic acid has also been used to some degree in biodegradable polymers, and as an electroplating bath additive, mordant, and textile and leather auxiliary [Ashford 2001, CMR 2001d]. In 1998, approximately 5 million pounds of lactic acid-containing polymers were consumed [CMR 2001d]. There are many potential derivatives of lactic acid, some of which are new chemical products, and others that represent biobased routes to chemicals currently produced from petroleum.

Improvements in fermentation and separation technologies have dramatically driven down the cost of production from approximately $1.00 per pound to $0.50 or less per pound. Future technology advancements could further decrease production costs of lactic acid to as low as $0.25 per pound, similar to the way ethanol production costs have been reduced through improvements in fermentation and separation processes. Considering the nature of lactic acid and ethanol fermentation, lactic acid could potentially be produced for costs similar to ethanol ($0.10-0.15 per pound). The chief difference is the higher costs to separate and purify lactic acid compared to ethanol.

Extensive R&D has and continues to be placed on lactic acid fermentation and separation technology. Projects co-funded by DOE are focused on microorganisms designed to utilize both C5 and C6 sugars in the fermentation. This would open up the use of lignocellulosic residues and energy crops (corn stover, wheat straw, rice straw, switch grass) as potentially lower cost feedstocks than C6 sugars derived from corn grain alone. Other DOE co-funded R&D continues to drive down costs in the separation and purification area.

Lactic Acid Derivatives

Table 3-6 lists the applications (current and potential), current market size and price, and 2020 market potential for lactic acid derivatives and products. In cases where the derivative is a new market, the market and price of the competing product is given.

Polylactide (PLA) is a thermoplastic polymer produced from lactic acid. The lactic acid is converted to lactide through a special condensation process. The lactide is then purified and ring-opening polymerization performed using a solvent-free melt process [CD 2002].

In April 2002, Cargill Dow LLC started up their first large-scale PLA plant in Blair, Nebraska. The plant has a 300 million pound capacity and demand for NatureWorks™ PLA has been so strong that Cargill Dow is likely to begin construction of a second plant within a few years [CD 2000]. Cargill Dow projects a possible market of 8 billion pounds by 2020 [Forbes 2001].

PLA is cost-competitive with and offers performance properties equal to or greater than those offered by conventional polymers. It requires 30-50% less fossil fuel to produce than conventional petroleum-based polymers (see Table 3-7) [CD 2002]. When it has reached the end of its life, PLA can be melted down and reused or composted.

Table 3-6 Lactic Acid Platform

Chemical	Applications[1]	Current U.S. Applications Market[2] (M lb)	Market Price[3] ($/lb)	Potential 2020 Market Size[4] (M lb)
Lactic Acid	**Acidulant (food, drink), electroplating bath additive, mordant, textile/leather auxiliary**	**<5 (industrial uses)**	**$0.70-0.85**	**Expect GDP-like growth**
Polylactide	Film and thermoformed packaging, fiber and fiberfill applications.	Packaging: 21,289 Fiber/fiberfill: 2,769	$0.30-1.50	8,000
Ethyl Lactate	Solvent (blended with methyl soyate) or as chemical intermediate	8,000-10,000	$0.30-1.80	>1,000
Acrylic Acid	Acrylates (e.g., coatings, adhesives) (52% of global consumption), comonomer, superabsorbent polymers (32% of global consumption), detergent polymers	2,000	$0.48	Will require technology breakthrough
Propylene Glycol	Unsaturated polyester resins (surface coatings, glass fiber reinforced resins), antifreeze, solvent, humectant, manufacturing of plasticizers, hydraulic brake fluids, non-ionic detergents	1,100	$0.39-0.48	Will compete against conventional petroleum-based PG as well as biobased PG via the thermochemical route
Pyruvic Acid	Ethyl pyruvate (electronics cleaning solvent, fungicide), sodium pyruvate (fermentation media)	Small	High	Not projected
1-Amino-2-Propanol	Unknown	Unknown	Unknown	Unknown
Lactonitrile	Unknown	Unknown	Unknown	Unknown
Lactic Amide	Unknown	Unknown	Unknown	Unknown
Lactide	Unknown	Unknown	Unknown	Unknown
2,5-Dimethyl-1,4-Dioxane	Unknown	Unknown	Unknown	Unknown

[1] These are the applications targeted by the biobased chemical; some are current applications, others are new opportunities.

[2] This is the volume of market opportunities represented by the applications in the second column.

[3] This is the price of the current applications targeted by the biobased product and not the price of the biobased product.

[4] Authors' estimates of the biobased market in 2020 based on the state of the technology development and current U.S. applications market size. Sources: Ashford 2001, CMR 2002d, SRI 2001, CMR 2002f, ACC 2000, CNI 2002, CEH 2002, CMR 2001d

Table 3-7 Energy Consumed in Plastic Manufacturing

Polymer	Total Energy Consumed[1] (Btu/lb)
Low Density Polyethylene	34,173
Linear Low Density Polyethylene	31,163
High Density Polyethylene	34,433
Polypropylene	33,257
Polystyrene (general purpose)	37,368
High Impact Polystyrene	39,737
Polyethylene Terephthalate	33,378
Polylactide	21,844

[1] Includes the feedstock energy content and the energy consumed in the feedstock processing, conversion, and transport
Source: SRI 2001

Plastic packaging represents the largest single market for polymer resins. In 2000, over 21 billion pounds of thermoplastics were used in packaging. With physical properties equal or superior to those offered by conventional polymers, PLA has the potential to make inroads in this area [SRI 2001] (Table 3-8). Specifically, PLA polymer exhibits high stiffness, superior clarity and gloss, dead-fold, grease resistance, and unique flavor and aroma barrier properties [CD 2001a].

PLA also exhibits the most desired properties of natural fibers such as wool and synthetics such as polyester. This combination of properties opens up a breadth of textile applications including clothing, carpet tiles, diapers (acquisition distribution layers), upholstery, furnishings, filtration, and agriculture. PLA has a high dyeability, and in comparison with polyester in activewear displays better wicking properties.

Cargill Dow has teamed with Biocorp, Inc. to produce compostable PLA cold drink cups and other items to be used at large venues. PLA cups premiered at the Womadelaid Festival in Australia, and were used at the 2002 Winter Olympic Games in Salt Lake City, Utah. Compostable food service items allow for the composting of food scraps without the high costs of separating the food from the food service items, enabling cost savings of up to 35% compared to landfill options [CD 2001a].

Cargill Dow currently relies on corn grain for its glucose, but is working on fermentation organisms that convert pentose sugars to lactic acid. This would enable the use of lignocellulosic material such as corn stover and rice straw that are cheaper than corn grain. Lower production costs would increase cost-competitiveness while providing a higher value outlet for low-value agricultural residues.

Table 3-8 Thermoplastics used in Packaging in 2000

Thermoplastic	Quantity (M lb)	Percent
Low Density Polyethylene	2,643	12.4
Linear Low Density Polyethylene	4,502	21.1
High Density Polyethylene	7,432	34.9
Polypropylene	3,498	16.4
Polystyrene	1,296	6.1
Nylon	107	0.5
Polyvinyl Chloride	971	4.6
Other	841	4.0
Total	21,289	100.0

Source: SRI 2001

Ethyl lactate is another lactic acid derivative that has recently been commercialized. It is an environmentally-benign solvent with properties superior to many conventional petroleum-based solvents. It can also be blended with methyl soyate derived from soybean oil to create custom-tailored solvents for specific applications.

Up until the past couple of years, the use of ethyl lactate has been limited due to high production costs. Selling prices for ethyl lactate have ranged between $1.50 and $2.00 per pound, compared to $0.90-$1.70 per pound for conventional solvents [IPP 1998]. DOE has co-funded lactic acid separations technology involving the use of electrodialysis, advanced membranes, and reactive separations capable of converting the lactic acid salts made during fermentation directly to ethyl lactate. With advances in lactic acid fermentation, separations and conversion technologies, production costs have been driven down as low as $0.85 [CE 1998].

Between 8 and 10 billion pounds of solvents are used in the U.S. annually, and it has been suggested by industry experts that ethyl lactate could replace conventional solvents in more than 80% of these applications [IPP 1998]. Ethyl lactate is currently being used by Vertec Biosolvents Inc. in soy oil-solvent blends. Applications targeted by Vertec Biosolvents include conventional solvents that are under environmental scrutiny such as methylene chloride, methyl ethyl ketone, and N-methyl-2-pyrrolidone [CMR 2002].

Other derivatives of lactic acid are shown in Figure 3-10. Acrylic acid, pyruvic acid, and propylene glycol are currently produced from petroleum and could potentially be produced from lactic acid. 1-Amino-2-propanol, lactonitrile, lactic amide, lactide, and 2,5-dimethyl-1,4-dioxane represent new product opportunities.

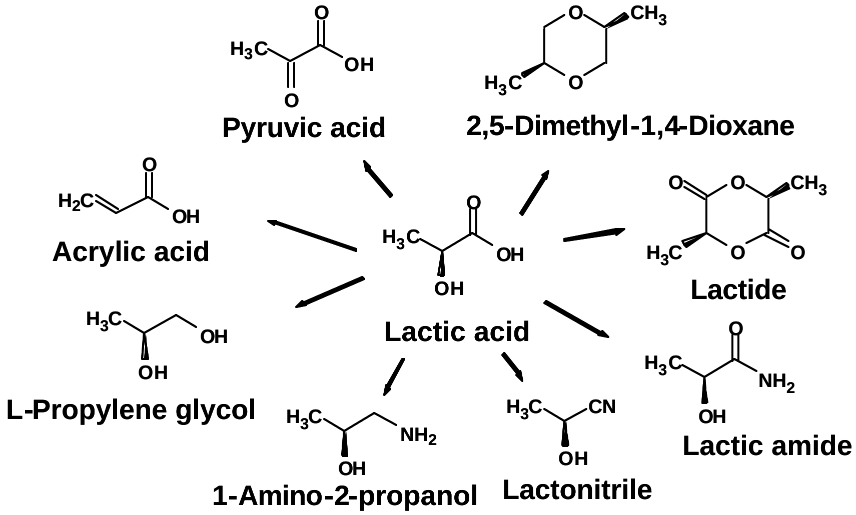


Figure 3-10 Potential Derivatives of Lactic Acid [PNNL 2002]

At about 2 billion pounds of production annually, **acrylic acid** is an attractive target for new biobased products [ACC 2000]. Modern production of acrylic acid is carried out through gas-phase catalytic oxidation of propylene via acrolein [CNI 2002]. Conversion of lactic acid to acrylic acid would require either the enzymatic or thermochemical dehydration of lactic acid. Researchers have attempted to develop a biobased route to acrylic acid, but have not yet found an economical process. In order to be competitive with current processes, the biobased route would have to yield a selling price of around $0.48 per pound [CNI 2002].

Propylene glycol is a commodity chemical with domestic production of about 1.1 billion pounds. It is currently produced by hydration of propylene oxide along with small amounts of di- and tripropylene glycols. Although it is possible to convert lactic acid to propylene glycol, it is also possible to thermochemically produce it from sugars. The thermochemical sugar route is more advanced and is projected to be cost-competitive with the petroleum-based propylene route. Production of propylene glycol from lactic acid may also be a viable route.

Pyruvic acid is a small-volume chemical whose derivatives are used in a variety of applications from emulsifiers to pharmaceuticals. It is currently produced through the hydrolysis of acetyl cyanide or by reacting tartaric acid with potassium hydrogen sulfate, but with advances in process chemistry it could be produced biochemically. Researchers at the National Institute of Advanced Industrial Science and Technology have discovered that pyruvate decarboxylase, the enzyme that catalyzes the decarboxylation of pyruvic acid to acetaldehyde and carbon dioxide at pH 7, can catalyze the reverse reaction at pH 11 [CE 2001]. Work is on-going to investigate the process.

Succinic Acid Fermentation Platform

Succinic acid (SA) and its salts form a platform from which many chemicals can be produced. Industrial SA is currently produced from butane through maleic anhydride, and food-grade succinic acid is produced through older fermentation and separation technology. Both routes are costly and this has limited use of SA to specialized areas. Consequently, the world market is small at 33 million pounds per year.

Succinic acid can also be produced through the fermentation of glucose. Most fermentation organisms are not tolerant of acidic conditions and the fermentation is typically neutralized, producing a salt of succinic acid. Conventional separation and recovery involves filtration to separate the solid cell mass, and re-acidifying of the succinate salt to form free succinic acid while precipitating out a salt.

There has been considerable research over the past 5-10 years to develop improved microorganisms and separations technology to reduce the overall cost of biobased succinic acid. Much of this has been co-funded by DOE. Research has resulted in the development of *Escherichia coli* strain AFP111, a microorganism with greatly improved productivity. Fermentation using AFP111 has recently been successfully tested at commercial scale.

Separations research has resulted in the development of a two-stage desalting and water-splitting electrodialysis system that concentrates, purifies, and acidifies the succinic acid. The base is recycled back to the fermentation where it is used for neutralization, eliminating the generation of gypsum salt, a typical undesired neutralization by-product that must be disposed of or sold [CRADA 1999].

In 1992, fermentation production costs for SA ranged from $1.50 to $2.00 per pound. Advances in fermentation and especially separation technology for the biobased route have reduced the potential production costs to about $0.50 per pound. Ongoing and further advances could significantly reduce the cost of biobased succinic acid even more.

Commercialization of these low-cost routes would have a significant impact on the demand for succinic acid and expand current markets as well as open up new markets for the acid and its derivatives. It is anticipated that the new low-cost biobased technology will be commercialized within the next 1-3 years.

Succinic Acid Derivatives

The real promise of succinic acid lies in its derivatives (see Table 3-9). Routes from succinic acid to chemicals in the first group shown in Table 3-9 have been researched through a DOE co-funded collaboration involving multiple national laboratories and Applied CarboChemicals, Inc. Applied CarboChemicals is now the main company behind the development of succinic acid derivatives and holds patents on the use of succinate salts as deicers and herbicide additives [Berglund 2001, Coleman 2001].

Other companies are now showing strong interest in the production of biobased succinic acid and its derivatives. Michigan Biotechnology Institute and Tate & Lyle have recently developed their own improved microorganisms for cost-effective fermentation and separation of succinic acid.

With the current production cost of succinic acid, derivatives such as THF, BDO, GBL, NMP, 2-pyrrolidone, and succinate salts are either cost-competitive or nearly cost-competitive with their fossil-based counterparts. Table 3-10 compares the cost of succinic acid derivatives with fossil counterparts.

Table 3-9 Succinic Acid Derivatives

Chemical	Current Applications/ Derivatives[1]	Current U.S. Market[2] (M lb)	Market Price[3] ($/lb)	Potential 2020 Market Size[4] (M lb)
Succinic Acid	**Surfactants/detergents, ion chelator (electroplating), food, pharmaceuticals, antibiotics, amino acids, and vitamin production**	**Small (world production is 33 M lb)**	**$2.70-4.00**	**GDP-like growth**
Tetrahydrofuran (THF)	Solvent and key ingredient of adhesives, printing inks, and magnetic tapes	255	$1.55	>50?
1,4-Butanediol (BDO)	THF, polybutylene terephthalate, GBL, solvent, coating resins, and chemical and pharmaceutical intermediates	680	$0.65-0.90	>30?
γ-Butyrolactone (GBL)	Solvent, 2-pyrrolidone, N-vinyl-2-pyrrolidone, polyvinylpyrrolidone, agrichemicals, pharmaceuticals, dyes, textiles finishing, printing, epoxies	105	*	*
N-Methyl Pyrrolidone (NMP)	Chemical synthesis solvent, selective solvent (aromatics/acetylene/ butadiene extraction), solvent (paint removers, polyimide coatings)	80	$1.34 (reclaimed) $1.85 (virgin)	Could be displaced by ethyl lactate
2-Pyrrolidone	Plasticizer/emulsifier, selective solvent (acetylene, acrylonitrile production), process solvent (pharmaceutical manufacture)	>65	Unknown	*
Succinate Salts	Deicing compounds	Road: 200	$0.02	Could replace 100% of airport deicers
		Airport: 10	$0.46-0.88	
	Herbicide ingredient	Small	Unknown	Small
Bionolle 4,4 polyester	Thermoplastic polymer applications	25,000-60,000	$0.30-1.50	>4,000?

Table 3-9 Succinic Acid Derivatives

Chemical	Current Applications/ Derivatives[1]	Current U.S. Market[2] (M lb)	Market Price[3] ($/lb)	Potential 2020 Market Size[4] (M lb)
Adipic Acid	Alkyd resin comonomer, food buffering agent, starch crosslinking agent, polymers (polyamides, polyester, etc.)	1,960	$0.625-0.775	Will require technology breakthrough
Succinamide	Unknown	Unknown	Unknown	Unknown
1,4-Diaminobutane	Polyamide 46 (automotive/electronic/ domestic appliance components)	Small	Unknown	*
Ethylenediamine-disuccinate	Replacement for EDTA (ethylene diamine tetraacetic acid)	175	$0.40 (~40% liquid) $1.40 (crystalline)	*
DL-Malic Acid	Aluminum anodizing reagent, sequesterant, preservative (cosmetics, toiletries, pharmaceuticals), reagent (chrome plating, electrodeless nickel coating, textile finishing)	20	0.81-0.84	*
Maleic Anhydride	~50% used in unsaturated polyester resins (fiberglass composites), 1,4-BDO, THF, GBL, plasticizers, surface coatings, agrochemicals, lubricants, fumaric acid, malic acid	546	0.32-0.45	Small
Fumaric Acid	Polymers (alkyd/unsaturated polyester resin, styrene-fumarate copolymer)	35	$0.82-0.85 food grade	*
Dibasic Esters	degreasers	50	Unknown	*

*not projected

[1] These are the applications targeted by the biobased chemical; some are current applications, others are new opportunities.
[2] This is the volume of market opportunities represented by the applications in the second column.
[3] This is the price of the current applications targeted by the biobased product and not the price of the biobased product.
[4] Authors' estimates of the biobased market in 2020 based on the state of the technology development and current U.S. applications market size.

Sources: CMR 2002c, CMR 2002d, Ashford 2001, C&EN 2001b, Berglund 2001, Rossell 1991, AMB 1999, CNI 2002

Table 3-10 Price Comparisons Between Succinic Acid and Its Fossil Competitors

Succinic Acid Derivative	Precursor(s)	Fossil Precursor Selling Price ($/lb)	Succinic Acid Production Cost ($/lb)
Tetrahydrofuran	BDO	$0.65-0.90	$0.25-0.50
	Maleic anhydride (MA)	$0.40-0.46	
1,4-Butanediol (BDO)	Butane → **MA** → BDO	$0.40-0.46	
	Acetylene + Formaldehyde	$0.21 (F)	
	Syn gas + allyl alcohol	----	
γ-Butyrolactone (GBL)	Maleic anhydride	$0.40-0.46	
	BDO	$0.65-0.90	
N-Methyl Pyrrolidone	GBL + methylamine	----	
2-Pyrrolidone	GBL + ammonia	----	
Succinate Salts[1]	Highway: NaCl[2]	$0.02	
	Highway: Calcium magnesium acetate[2]	$0.46	
	Aviation: **Propylene oxide** → propylene glycol	$0.64	

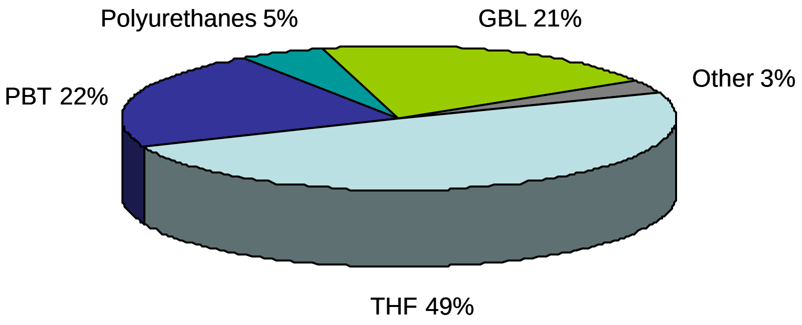
[1] Succinate salts are compared to the products they would displace in the deicer market.
[2] This is the product succinate salts will compete against, and not the precursor of the competitive product.
Bold font indicates the precursor for which the selling price is provided.

Sources: ACC 2000, CMR 2002d, C&EN 2001b

1,4-Butanediol and its derivatives (THF, GBL, NMP, 2-pyrrolidone) represent a market ripe for the introduction of a competitive biobased route (see Figure 3-11). Demand and growth are high (5-6% annually), supply is tight, and raw material costs for fossil-derived butanediol have increased sharply over the past two years [CMR 2002c, CMR 2001e].

Most domestic BDO is produced by the Reppe process in which acetylene is reacted with formaldehyde. It can also be produced via propylene oxide or maleic anhydride [CNI 2002]. The DOE-industry-laboratory collaboration has developed a two-step process to convert biobased succinic acid to BDO and a process to produce a mixture of 2-pyrrolidone and NMP [CRADA 1999].

An economic analysis of BDO production has shown that the biologically derived succinic acid process (BDSA) has the potential to dramatically decrease production costs of BDO (see Table 3-11). Added benefits include reduced materials of construction cost due to the lower corrosivity of succinic acid and lower energy requirements. Improvements in separations technology have further reduced process energy needs.



1999 U.S. 1,4-Butanediol Production: 730 million pounds

Figure 3-11 2001 U.S. 1,4-Butanediol Consumption [CMR 2002c, ACC 2000]

Table 3-11 Economic and Energy Analyses of Multiple Routes to 1,4-Butanediol

Process	BDSA	Reppe	Kuraray/ARCO	Davy McKee
Raw material	Corn sugar	Petroleum, natural gas (acetylene/form aldehyde)	Syngas (propylene oxide)	Butane/maleic anhydride (petroleum)
Estimated production cost	\$0.43/lb BDO	\$0.66/lb BDO	\$1.14/lb BDO	\$0.89/lb BDO
Energy Use (per lb BDO)	36,000 Btu	42, 000 Btu	39,000 Btu[1]	-----

[1] Estimated from utilities cost.
Source: CRADA 1999

Tetrahydrofuran (THF) is an important reaction solvent, and is also used in the manufacture of polytetramethylene glycol (building block for urethane elastomers, polyurethane fibers, elastomers). Demand for THF is strong and production is projected to grow at an average annual rate of 5.2% through 2005 [CMR 2002c]. It is currently manufactured by the cyclodehydration of BDO and accounts for 48% of total BDO consumption. Research has shown that a mixture of THF, GBL, and BDO can be produced from succinic acid in a single step [CRADA 1999, CMR 2002c].

Gamma-butyrolactone (GBL) is currently manufactured from either 1,4-butanediol or maleic anhydride (both fossil-based), but several processes have been developed to catalytically reduce succinic acid to GBL. Depending on the catalyst selected, succinic acid can be converted to solely GBL or to a mixture of GBL, BDO, and THF in a single step [CRADA 1999].

Other commodity chemicals that can be manufactured from succinic acid include **N-methyl pyrrolidone and 2-pyrrolidone**. Current production is via GBL and methylamine to NMP or GBL and ammonia to 2-pyrrolidone [Ashford 2001]. The biobased routes developed or under development catalytically convert succinic acid or other derivatives to a mixture of NMP, 2-pyrrolidone, and in some cases GBL [CRADA 1999].

Showa Denko in Japan has introduced a **biodegradable 4,4-polyester** polymer (Bionelle) with a range of compositions utilizing some combination of succinic acid, adipic acid, BDO, and ethylene glycol. It is potentially a very versatile plastic material with uses and potential markets similar to PLA [SCI 2002]. Sales of Bionelle have been hindered by the current high cost of manufacturing. Low-cost biobased production routes to BDO and succinic acid could favorably impact this situation.

Succinate salts (calcium, magnesium, diammonium, ammonium) show near-term market potential. Succinate salts are produced through the neutralization of succinic acid, an intermediate step in the production of succinic acid by fermentation. Two key applications identified are herbicide additives or de-icing compounds for roads, aircraft, and airport runways. Herbicide use is high, but the active ingredients (herbicide and succinate salt enhancer) comprise only a small amount of the product, between 0.5 and 3.0 weight percent.

In 1990, approximately 10 million pounds of salt (NaCl) was used on roads and highways and around 200 million pounds of aviation de-icers are currently used each year [Berglund 2001, C&EN 2001b]. Both groups of deicers are under pressure from environmental groups. Federal and State aviation and highway agencies are also looking for deicers with improved performance and reduced corrosiveness. Succinate salts are ideal for this purpose as they offer improved ice penetration characteristics while being less damaging to concrete, asphalt, metals, and the environment.

The second group of succinic acid derivatives in Table 3-9 contains chemicals that have the potential to be made from succinic acid, but have not been researched as extensively as the first group. Adipic acid is the most promising with a market of nearly 2 billion pounds, but is now produced at a low cost ($0.62-0.78 per pound) from petroleum. Improved technology and novel chemistries would be required to make biobased adipic acid competitive with the petroleum-based route. Markets for the remaining compounds are virtually unexplored.

3-Hydroxypropionic Acid

The fermentation of glucose to 3-hydroxypropionic acid (3-HP) is just now being actively investigated by Cargill, Inc. Many high volume products can be made from 3-HP creating the potential for a platform intermediate similar to lactic acid and succinic acid (Table 3-12).

The synthesis of acrylic acid, and the process for obtaining the salts and esters of acrylic acid from 3-HP have been demonstrated in the laboratory. Other derivatives under consideration include acrylamide, 1,3-propanediol, malonic acid esters, and acrylonitrile [Gokarn 2002]. As with polylactide, there is no commercially-viable production route of 3-HP from fossil fuel feedstocks.

The conversion of 3-HP to acrylic acid is expected to be "easier" and may require less energy than the oxidation of propylene to acrylic acid [Gokarn 2002]. As new conversion technologies are developed, the challenge will be to make them cost-competitive with the current fossil-based routes to acrylic acid.

1,3-Propanediol

1,3-propanediol, together with terephthalic acid, is used to produce polytrimethylene terephthalate (PTT). PTT is a polymer with remarkable "stretch-recovery" properties, and is used in apparel, upholstery, specialty resins, and other applications where properties such as softness, comfort-stretch and recovery, dyeability, and easy-care are desired. It is currently manufactured by Shell Chemical (CORTERRA Polymers) and DuPont (Sorona® 3GT). Studies have shown that the properties of DuPont's Sorona® surpass nylon and polyethylene terephthalate (PET) in fiber applications and polybutylene terephthalate and PET in resin applications such as sealable closures, connectors, extrusion coatings, and blister packs [DuPont 2002].

PTT polymers currently on the market are made using fossil-based 1,3-propanediol. However, Genencor International and DuPont have been collaborating to develop the metabolic pathway in *E. coli* to produce 1,3-propanediol directly from glucose at a lower cost. It is expected that commercial production of biobased 1,3-propanediol will commence in 2003 [DuPont 2000].

Based on its use in PTT, 1,3-propanediol has a potential 2020 market of 500 million pounds. The successful penetration of PTT into the polymers market will hinge on both its performance and economics. In specialty applications, polymers can sustain higher monomer costs while still meeting demand and making a profit. In commodity applications, the cost of 1,3-propanediol will have to approach the monomer prices for PTT's market competitors—PET and nylon—which range from $0.20 to $0.30 per pound.

Table 3-12 Derivatives of 3-Hydroxypropionic Acid

Chemical	Uses[1]	Current Market[2] (M lb)	Market Price[3] ($/lb)	Potential 2020 Market Size[4] (M lb)
Acrylic acid	Acrylates (e.g., coatings, adhesives) (52% of global consumption), comonomer, superabsorbent polymers (32% of global consumption), detergent polymers	2,000	$0.48	Technology just now being developed
Acrylonitrile	Acrylic fibers (carpets, clothing), acrylonitrile-butadiene-styrene and styrene-acrylonitrile (pipes and fittings, automobiles, furniture, packaging), nitrile rubber copolymers, adiponitrile, acrylamide	3,130	$0.31-0.37	Technology just now being developed

Table 3-12 Derivatives of 3-Hydroxypropionic Acid

Chemical	Uses[1]	Current Market[2] (M lb)	Market Price[3] ($/lb)	Potential 2020 Market Size[4] (M lb)
Acrylamide	Polyacrylamide, comonomers (styrene-butadiene latex, acrylic resins, and many others)	206	$1.76-1.86	Technology just now being developed
1,3-Propanediol	Polyethylene terephthalate, polybutylene terephthalate, and nylon applications	Small	$0.30-0.50	Technology just now being developed
Malonic acid	Blowing agent (foamed plastics), silver plating brightening agent, tanning auxiliary	<1	High	Technology just now being developed

[1] These are the applications targeted by the biobased chemical; some are current applications, others are new opportunities.
[2] This is the volume of market opportunities represented by the applications in the second column.
[3] This is the price of the current applications targeted by the biobased product and not the price of the biobased product.
[4] Authors' estimates of the biobased market in 2020 based on the state of the technology development and current U.S. applications market size.

Sources: ACC 2000, CNI 2002 CMR 2002e, Ashford 2001

Butanol Fermentation and Derivatives

Butanol is a platform chemical with several large volume derivatives, and is used as a solvent and in plasticizers, amino resins, and butylamines (see Table 3-13). Butanol can also be used as a biobased transportation fuel and is more fuel efficient than ethanol on a volume basis in this application.

In 1999, domestic demand for butanol was 1.85 billion pounds and it is projected to increase 3% per year [CMR 1999a]. During the early 20th century the primary method of butanol production was glucose fermentation with *Clostridium acetobutylicum* to produce a mixture of acetone, butanol, and ethanol. The butanol yields were low (15 weight %) and the process was complex and difficult to control, leaving the door open for development of petrochemical routes to butanol. The primary petrochemical route used today involves the hydrogenation of n-butyraldehyde.

The DOE SBIR program is funding research to improve the biobased route to butanol and make it cost-competitive with the petroleum-based route. Researchers are attempting to increase butanol yield by using improved bacteria strains, employing advanced reactor technology, and separating the organic acid production and organic acid-to-alcohol phases into different vessels. A material and energy balance predicts that a yield of 2.5 gallons of butanol per bushel of corn could be achieved [DOESBIR 2002].

Table 3-13 Butanol Applications and Derivatives

Chemical	Applications[1]	Current U.S. Market[2] (M lb)	Market Price[3] ($/lb)	Potential 2020 Market Size[4] (M lb)
n-Butanol	Direct uses: solvent, plasticizer Derivatives: Polymers and resins (butyl acrylate, methacrylate), solvents (glycol ethers, butyl acetate), amino resins, butylamines	1,850	$0.55	Could be significant

[1] These are the applications targeted by the biobased chemical; some are current applications, others are new opportunities.
[2] This is the volume of market opportunities represented by the applications in the second column.
[3] This is the price of the current applications targeted by the biobased product and not the price of the biobased product.
[4] Authors' estimates of the biobased market in 2020 based on the state of the technology development and current U.S. applications market size.

Sources: Ashford 2001, CMR 1999a, CMR 2002d

PHA Polymers via Fermentation

PHAs are a family of natural polymers produced by many bacterial species for carbon and energy storage. They are extremely versatile and can be used in a broad range of applications. Their performance exceeds that of PLA, and PHAs could capture a large share of the plastics market if they could be produced at a competitive cost.

Cost-effective fermentation production routes have been pursued since the 1970s by ICI, Zeneca, and to some degree by Monsanto and others. Bacterial fermentation of PHAs, specifically poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), has been performed commercially by Zeneca and then Monsanto and under the trade name Biopol™ in the 1990s. PHBV has been used to make plastic bottles and coated paper [JIE 2001]. However, PHBV could not compete with conventional petroleum-based plastics using the fermentation and separation technology available at the time.

Metabolix has since developed lower cost fermentation technology for PHAs. The company claims this advanced fermentation technology would permit large-scale commercial production for under $1.00 per pound. Production at this cost could open up a significant market for fermentation-based PHA. Metabolix launched its first commercial fermentation-based PHA product in 2002.

A still lower-cost route to PHAs is genetic modification of plants to produce the final polymer directly in plants. This approach was pursued by Monsanto (and others) and is currently being co-funded by DOE in a collaborative research project led by Metabolix. This technology is also discussed in Section 3.3.9, Plants as Factories.

Fermentation-Derived L-Lysine

L-lysine is an amino acid used as an animal feed additive, raw material for pharmaceutical salts and peptide drugs, and in diagnostic aids. The U.S. imports most of its supply from China where L-lysine is produced from cornstarch and molasses. Markets for L-lysine are relatively small. An improved process is necessary to make domestic production economically competitive with imported lysine.

3.3.2 Fermentation of 5-Carbon Sugars (Xylose) to Bioproducts

Pentose sugars such as xylose have thus far been an untapped resource. The microorganisms researched extensively in the past have preferred glucose over xylose and it is only recently that progress has been made in developing microorganisms capable of utilizing both pentose and glucose sugars.

It is much easier and less costly to hydrolyze biomass pentose sugars. By developing microorganisms that utilize pentose sugars alone or in combination with glucose, the overall economics of biobased products will improve by enabling greater utilization of the available biomass.

There is active research in this area. Improvements in C5 and C6 metabolism will further reduce the cost of biomass sugar fermentation and have a significant impact on the economics of the lactic acid and succinic acid platforms as well as other biobased products. Some potential xylose derivatives are shown in Table 3-14 and discussed below.

Itaconic Acid

Use of itaconic acid has been limited by the high costs of production from petroleum, but it can be fermented from xylose offering a lower cost route and the potential for expanded use. With lower-cost production processes, itaconic acid could compete with methyl methacrylate (MMA) and other acrylates as well as in the pressure-sensitive adhesives (PSA) market and other applications. Combined markets for acrylate and MMA are 1.8 billion pounds, and annual growth is projected to be 2-3% [ACC 2000, CNI 2002]. MMA is dependent on the housing and automotive sectors, which have been experiencing steady growth in the U.S.

Furans

Furans such as furfural, furfuryl alcohol, and 2-hydroxymethyl tetrahydrofuran can be fermented from xylose. Production of furans in the U.S. is minimal or non-existent, primarily due to cost and cheap imports from countries such as China where they are produced from corncobs. The last U.S. producer of furfural, for example, closed several years ago. As technologies for pretreatment and pentose-utilizing microorganisms improve, the cost of producing furans domestically may again become competitive with imported products.

3.3.3 Thermochemical Conversion of Sugars to Bioproducts

In addition to fermentation, biomass sugars can be upgraded to valuable products using thermochemical methods. Some thermochemical technologies such as the production of sorbitol from glucose have been in use for over 50 years. In recent years, the production of higher value-added products from biomass sugars has been advancing rapidly due to the development of new and improved catalysts. Much of the focus on sugars thermochemistry has been on sorbitol, levulinic acid, and their derivatives.

Sorbitol Derivatives

Sorbitol is produced through the hydrogenation of D-glucose. Over 616 million pounds are produced in the U.S. each year and consumption is almost equally split between personal care products and foods and confections [CMR 2001f]. The markets for sorbitol are well developed and growth is projected to be low. However, new catalysts and technologies for the conversion of sorbitol to glycols are creating new opportunities for bioproducts.

Propylene glycol (PG), ethylene glycol (EG), and glycerol are often collectively referred to as glycols and are used in many industrial and consumer applications (see Table 3-15). Glycol derivatives include numerous polyester resins and copolymers, polyethers, and alkyd resins.

Table 3-14 Xylose Fermentation Derivatives

Chemical	Applications[1]	Current U.S. Market Size[2] (M lb)	Market Price[3] ($/lb)	Potential 2020 Market Size[4] (M lb)
Itaconic Acid	Current: Aluminium anodizing reagent, reactive comonomer, carboxylated styrene-butadiene copolymers	~7.5	High	Significant if technology is successful
	Potential: MMA	1,500	$0.48-0.56	
	Potential: Acrylic PSA	300	$2.00-4.00	
Furfural	Comonomer, selective solvent (butadiene/aromatics extraction), solvent (fatty acid/wood rosin separation), numerous derivatives	68	$0.79	Not projected
Furfuryl Alcohol	Gel retarder (casein/protein glues), non-reactive epoxy resin diluent, resins	19	$0.38-0.44	Not projected
2-Hydroxymethyl Tetrahydrofuran	Unknown	Unknown	Unknown	Unknown

[1] These are the applications targeted by the biobased chemical; some are current applications, others are new opportunities.

[2] This is the volume of market opportunities represented by the applications in the second column.

[3] This is the price of the current applications targeted by the biobased product and not the price of the biobased product.

[4] Authors' estimates of the biobased market in 2020 based on the state of the technology development and current U.S. applications market size.

[5] Includes tetrahydrofurfuryl alcohol, a derivative of furfuryl alcohol.

Sources: ITA 2001, CNI 2002, ACC 2000, ASI 2000, Ashford 2001, CEH 2002

Glycols represent the largest market for sorbitol derivatives. In 1999, a combined seven billion pounds of glycols were produced in the U.S [ACC 2000, CEH 2002]. The antifreeze market is essentially flat, but others such as non-ionic detergents and polyesters are growing rapidly.

Current production of propylene and ethylene glycol is petroleum-based. Production of propylene glycol is by hydration of propylene oxide. Ethylene glycol is manufactured by a direct oxidation route [CNI 2002]. Glycerol is the by-product of many processes involving animal or vegetable lipids. The reactions used to produce glycerol —hydrolysis, transesterification, dehydration, hydrogenation—depend on the specific feedstock.

There is a lack of new capacity for both ethylene and propylene glycol and it has been estimated that supplies could be short as soon as 2003 or 2004. This could be fortuitous for the entrance of biobased glycol into the market. The Pacific Northwest National Laboratory (PNNL) is developing a cost-competitive biobased route to propylene glycol, which could also be modified for the production of ethylene glycol and glycerol. This process is based on the catalytic hydrogenolysis of sorbitol. Process development is nearing completion and could be used to generate new capacity.

Table 3-15 Thermochemical Derivatives of Sorbital

Chemical	Uses	Market[1] (M lb)	Market Price[2] ($/lb)	Potential 2020 Market Size[3] (M lb)
Ethylene Glycol	Solvents, surface coatings, printing inks, pharmaceuticals, cosmetics, heat transfer fluids, humectants, plasticizers, antifreeze	5,950	Polyester: $0.20-0.22 Anti-freeze: $0.16-0.19 Industrial Grade: $0.25-0.275	Small
Propylene Glycol		1,100	$0.68-0.71	>500
Glycerol		428	$0.90-1.10	Small
Isosorbide	Active ingredients in diuretic and anti-anginal drugs	Small	Unknown	If technology is successful, could reach 100-300

[1] This is the current market of the petroleum-based chemicals

[2] These are the prices of the petroleum-based chemicals.

[3] This is the potential market of the biobased chemical as estimated by the authors.

Sources: ACC 2000, CMR 2002d, CEH 2002, Ashford 2001

A derivative of sorbitol that is currently produced, although in very small amounts, is **isosorbide**. Current production uses aqueous mineral acids to catalyze the dehydration (loss of two water molecules) of sorbitol. Yields and catalyst specificity are low and the use of aqueous acids requires a very energy-intensive and expensive separation process to recover the product. The use of a batch process rather than a continuous process also contributes to higher operating costs.

Researchers at PNNL are developing a continuous process for isosorbide using solid acid catalysts. The solid catalyst has a higher specificity and gives higher yields, creating a more economical process. It is far easier to separate isosorbide from the solid catalyst than from the water-soluble mineral acids. The continuous process will further lower production costs.

Thus far, isosorbide has been limited to specialty applications, but lower costs and continuous production could lead to applications in larger markets, such as polymer additives. It has been shown that the addition of isosorbide in small amounts (e.g., 4 weight %) to polyethylene terephthalate (PET) can enhance properties such as strength-to-weight ratio.

DuPont holds all of the patents for the use of isosorbide with PET and their market studies have indicated that the 2020 market for isosorbide could be as large as 100 million pounds per year. Beyond 2020, there is the potential for significant market expansion. Based on the displacement of 4% of current PET production (see Table 3-8) with isosorbide, the isosorbide market could reach nearly 300 million pounds. Additionally, it may be found that higher volumes of isosorbide can be added to PET and other polymers, increasing the potential market.

Another chemical that could be made from sorbitol through dehydration (loss of one water molecule) is D-1,4-sorbitan. The potential of this chemical has yet to be explored.

Levulinic Acid Platform

Levulinic acid has been well explored as a platform intermediate. Current production is fossil-based and due to high costs ($4.00-6.00 per pound), the use of levulinic acid and its derivatives has been limited to high-value specialty applications such as a chiral reagent, biologically active material, corrosion inhibitor, and others. The worldwide market is only one million pounds per year [BCOTA 1999, RCR 2000].

With support from DOE, New York State Energy Research & Development Authority (NYSERDA), EPA, and other organizations, the Biofine process was developed to utilize lignocellulosic material such as paper mill sludge, municipal solid waste, paper and wood wastes, and agricultural residues and convert it to levulinic acid using high temperature, dilute-acid hydrolysis. Approximately 0.5 pounds of levulinic acid is produced per pound of cellulose processed [BCOTA 1999]. Co-products include furfural, formic acid, and a solid residue that can be used as fuel.

The manufacturing cost for levulinic acid production using this technology could be less than $0.50 per pound and possibly less than $0.10 per pound (see Table 3-16). Levulinc acid can be used in existing or new applications or converted to other chemicals. Chemicals derived from LA that were explored by the DOE project include methyl tetrahydrofuran (MTHF), δ-amino levulinic acid (DALA), and diphenolic acid.

MTHF is manufactured by the hydrogenation of furfural and is currently used to produce primaquine, an antimalarial drug. Its potential as a transportation fuel extender has been explored by DOE. MTHF can be blended in gasoline up to 70% by volume without adverse engine performance and the fuel does not exhibit decreased miles per gallon efficiency. By displacing gasoline, MTHF could contribute to reducing dependence on foreign oil.

The high costs of levulinic acid production and the multi-step process required to produce MTHF have prohibited the development of MTHF as a gasoline additive. The single-step process developed by PNNL has significantly reduced costs and made it a viable alternative to MTBE. However, ethanol has replaced MTBE as the preferred oxygenate and is firmly established in the transportation marketplace. MTHF will have to compete with ethanol's $0.80 per gallon production cost in order to penetrate the transportation fuel additive market.

DALA is the active chemical in a new group of herbicides and pesticides with a projected market of 200-400 million pounds per year [DOE 2000]. It has also been found to be useful in a photodynamic therapy as a cancer treatment. The initial production process was demonstrated with high yields (>80%) and high-purity DALA (90%) [DOE 2000]. More recent improvements to the process have resulted in reduced generation of waste and enabled the use of several different solvents in the first step of the process.

Diphenolic acid (DPA) is an alternative to bisphenol A (BPA) which is used in polymers such as polycarbonates and as a comonomer in phenolic resins. Approximately 4.4 billion pounds of phenolic resins were produced in 2000, offering a large potential market for diphenolic acid, but only if it is cost-competitive with BPA, which is selling for just under a dollar per pound. The projected price for biobased DPA of $1.20 per pound is contingent upon a levulinic acid price of $1.00 per pound [RCR 2000, CMR 2002d].

Other potential derivatives of levulinic acid include tetrahydrofuran (THF), 1,4-butanediol (BDO), γ-butyrolactone (GBL), and n-methyl pyrrolidone (NMP). These were discussed previously under the succinic acid platform.

Table 3-16 Levulinic Acid Derivatives

Product	Use[1]	Current Price[2] ($/lb)	Current Market[3] (M lb/yr)	Potential LA Market (M lb/yr)
Methyl Tetrahydrofuran	Fuel extender	$0.13-0.18 ($0.80/gal)	30,800 (oxygenates)	(Challenging to penetrate oxygenate market)
δ-Amino levulinic acid	Biodegradable herbicide	Unknown	Unknown	200-400
Diphenolic acid	Monomer (Bisphenol A alternative)	$0.94	1,910	35
Tetrahydrofuran	Comonomer, solvent	$1.55	255	>50
1,4-Butandiol	Monomers	$0.65-0.90	680	>30

[1] These are the applications targeted by the biobased chemical; some are current applications, others are new opportunities.

[2] This is the price of the current applications targeted by the biobased product and not the price of the biobased product. This is the volume of market opportunities represented by the applications in the second column.

[3] This is the volume of market opportunities represented by the applications in the second column.

Sources: BCOTA 1999, Ashford 2001, ACC 2000, CMR 2002c, CMR 2002d, CNI 2002, USGS 2001

D-Gluconic Acid

D-gluconic acid is used as a sequestrant in alkaline dairy and brewery cleaners and its derivatives include dietary and animal feed supplements, an anaemia treatment drug, and food additives [Ashford 2001]. It is produced from glucose through anaerobic fermentation with *Aspergillus niger* to form sodium gluconate which is then acidified to yield gluconic acid. Selling prices range between $0.45 and $0.56 per pound, but a more direct route through oxidation may reduce production costs [CMR 2002d]. This route has yet to be explored.

Thermochemical Xylose Derivatives

The thermochemistries of 5-carbon sugars are the same as those used on 6-carbon sugars. For example, hydrogenation of xylose yields xylitol, the 5-carbon counterpart of sorbitol. From sorbitol, one can manufacture the glycols—ethylene glycol, propylene glycol, and glycerol. A catalyst under development at PNNL is very effective at cracking xylitol to **ethylene glycol, propylene glycol, and glycerol,** important commodity chemicals. Archer Daniels Midland, a company with an abundant supply of corn fiber, is interested in the PNNL-developed catalyst as a way to extract more value from the products of corn milling. Corn fiber has a high hemicellulose content which can be relatively easily hydrolyzed to xylose and other C5 sugars. In fact, the catalyst has been shown to produce greater yields of glycols starting from xylose than from glucose. Xylitol can also be converted to xylitan through dehydration and although its applications have not been explored, it could prove to be a valuable derivative as well.

Other thermochemical derivatives of xylose include D-xylonic acid and D-xylaric acid which are produced through oxidation. As with xylitan, their uses have not been investigated and will require additional analysis to determine whether they have market potential.

3.3.4 Oil and Lipid-Based Bioproducts

Thermochemical methods of conversion are becoming more and more sophisticated, expanding the breadth of chemistries possible for vegetable oils. Due to the versatility of vegetable oil-based products, this discussion concentrates on market segments rather than individual chemicals. Markets that utilize vegetable oil-based derivatives include lubricants and hydraulic fluids, solvents, polymers, resins, plasticizers, printing inks, adhesives, surfactants, cosmetics, pharmaceuticals, and numerous niche applications.

This report does not cover those markets that are well established and do not present significant growth for new industrial bioproducts. Examples of this would be the printing ink market where the use of soy-based inks has become common.

We are only beginning to recognize the potential for vegetables oils as new industrial products. Table 3-17 illustrates the current and potential uses of the oilseeds currently grown and those that are under development as industrial crops.

Lubricants and Hydraulic Fluids

The U.S. lubricant market is nearly 20 billion pounds per year [EIA 2000] (see Figure 3-12). Lubricants were originally manufactured from vegetable oils and animal fats but were displaced by petroleum-based lubricants in the late 1800's. They are used to reduce friction and wear, and for the transmission of force in mechanical equipment. They facilitate the effective operation of equipment in every sector of the economy.

Conventional petroleum-based lubricants exhibit a wide range of characteristics. Some of the properties used to characterize lubricants are viscosity, specific gravity, vapor pressure, boiling point, flash point, pour point, and lubricity. These characteristics depend on the oil formulation which has been tailored to meet the demands of the application.

Table 3-17 Comparison of Vegetable Oil Uses

	Lubricants& Hydraulic Fluids	Solvents	Printing Inks & Supplies	Paints, Varnishes, Waxes, Paint	Polymers, Resins, & Plasticizers	Adhesives	Fatty Acids/ Surfactants	Niche
Soybean	√	√	√	√	√	√	√	√
Sunflower	√				√			
Safflower	√				√			√
Rapeseed	√				√			
Crambe	√				√			
Castor	√			√	√			√
Cuphea							√	
Lesquerella	√			√	√			√
Linseed			√	√				√
Jojoba	√		√	√	√		√	√
Meadowfoam	√			√	√		√	√

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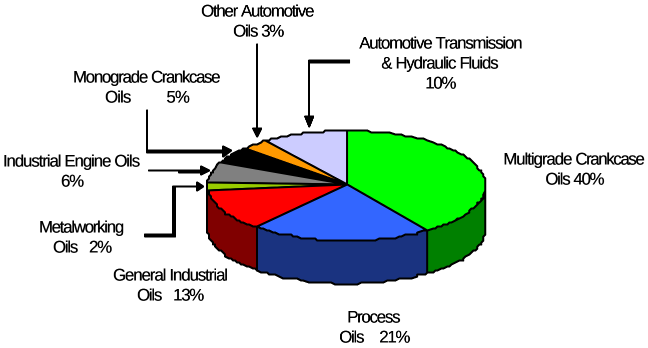

Total: 2.5 Billion Gallons (Approximately 20 Billion Pounds)

Figure 3-12 Total U.S. Sales of Lubricants [NPRA 2001]

Table 3-18 Typical Composition of Lubricants

Ingredient	Grease	Gear Oil
Base Oil	60-95%	75-95%
Thickener	0-20%	---
Solid Lubricant	0-20%	0-5%
Additive Package	0-10%	0-10%
Adhesives	0-20%	0-10%

Source: LLINCWA 2001

The typical composition of a petroleum-based lubricant is shown in Table 3-18. The main components of a lubricant are the base oil, thickeners, solid lubricants, and additives. Of particular interest is the base oil, which can be a mineral oil, synthetic oil, or vegetable oil and is used to impart lubricity to the product [LLINCWA 2001].

Vegetable oil-based lubricants are lower cost alternatives to petroleum-based lubricants. They show the potential to outperform conventional lubricants with a higher viscosity index, lower evaporation loss, and higher lubricity. They are also more readily biodegraded and less toxic to the environment— challenges faced by lubricant manufacturers today. Although they exhibit lower thermal, oxidative, and hydrolytic stability than conventional lubes, these problems can be overcome by additives or by modification of the vegetable oil.

Performance characteristics of vegetable oils are an extension of their fatty acid profiles. Saturated fatty acids freeze more easily than unsaturated fatty acids, limiting their performance in low temperature conditions. A vegetable oil-based lubricant will thus require a certain fatty acid composition to optimize performance at different conditions.

New technologies are being developed to increase oxidative stability by eliminating and/or reducing the number of double bonds and improving other performance properties. Genetic engineering of oil crops to create more favorable compositions for lubricants is also being pursued. For example, DuPont has modified soy to produce a very high oleic acid content (>70%) although this research was focused on health aspects. Other researchers are working on more modest changes (50%) that they believe will be sufficient for soy oil use in engine oils.

Some biobased engine lubricants are being introduced into the market, especially in less severe applications such as marine engines, through the use of antioxidant formulations. Metathesis chemistry (see the Polymers, Resins, and Plasticizers section) can be used to crack vegetable oil fatty acids and yield chemicals nearly identical to those being used today in high performance engine lubricants such as Mobil-1.

Vegetable Oil-Based Solvents

Between eight and ten billion pounds of solvents are used in the U.S. each year, representing a substantial target for vegetable oil-based solvents.

Methyl soyate is an excellent biobased solvent, and is produced by transesterifying soy oil with methanol resulting in a mixture of soy fatty acid methyl esters. Several biobased solvents containing methyl soyate have been introduced into the marketplace in recent years, fueled by demand for environmentally-benign products. These match or surpass the performance of some conventional solvents while being cost-competitive.

In 2001, only 1 million pounds of soybean oil was used in solvents. There is substantial room for growth in the use of methyl soyate and other vegetable oil-based products [USB 2001]. The acceptance of methyl soyate products by industrial manufacturers is based on performance as well as cost, and is anticipated to grow as rapidly as biobased solvent manufacturers can develop formulas for specific applications.

The properties of methyl soyate are potentially shared by other vegetable oil derivatives. Methyl soyate exhibits superior solvency, is readily biodegradable, and has a low toxicity compared with many other common chemicals. It is safer to store and handle than most conventional solvents due to its high flash and boiling points. Its only drawbacks are slow evaporation and insolubility in water. These can be overcome by blending with surfactants or co-solvents such as ethyl lactate.

Vertec Biosolvents, for example, blends ethyl lactate (see Section 3.3.1), methyl soyate, and d-limonene (from citrus fruits) to formulate VertecBio Gold and VertecBio Citrus solvents. These solvents represent an environmentally-friendly alternative to petroleum solvents. For example, they are being used to replace methylene chloride used for metal cleaning and finishing, methyl ethyl ketone used in ink cleaners, and N-methyl-pyrrolidinone (NMP). NMP is used in many applications (see Succinic Acid) and in 2001 was listed on California's Proposition 65. Some users of NMP have already substituted Vertec's solvents in their formulations. [CMR 2002]

The driving force behind products such as Vertec's is favorable economics. The methyl soyate blends compete with petroleum-based solvents not just because of performance and an environmentally-friendly profile; they are cost-competitive as well. Prices for methyl soyate and other common solvents are shown in Table 3-19.

Table 3-19 Selling Price of Common Solvents

U.S. Solvent Production	8-10 billion lb
Product	**Price**
Methyl soyate	$0.30-0.45/lb
Aqueous cleaners	$10/gal
Semi-aqueous cleaners	$30/gal
NMP	$1.50-1.80/lb
d-Limonene	Up to $0.40/lb
Methylene chloride	$0.30/lb
Trichloroethylene	$0.65/lb
Methyl ethyl ketone	$0.46/lb
Perchloroethylene	$0.35/lb

Source: USB 2002a

Oil-Based Polymers, Resins, and Plasticizers

The diversity of structure and inherent functionality of vegetable oils make them prime candidates for use in polymers and resins. The fatty acid chains in vegetable oils can be manipulated with a host of old and new chemistries to yield high performance products with desirable properties. Considering the 100 billion pound polymer market in the U.S. (see Table 3-20), there is a strong impetus for developing vegetable oils for this purpose.

The chemistries that are being used to functionalize vegetable oils to improve or enable their use in polymers include transesterification, epoxidation, hydroformylation, and metathesis. Transesterification and epoxidation are already being used to modify soy oil for use in industrial products. Hydroformylation and metathesis are well developed for use on petroleum feedstocks. The challenge will be to develop similar catalyst systems that are effective and efficient on vegetable oils.

Table 3-20 Soy Oil and Potential Markets for Vegetable Oils

Product	Current Market (M lb)	Price ($/lb)
Soy oil, crude	115	$0.21
Epoxidized soy oil		$0.48-$1.00
Polymers	100,000	
Polyurethane	5,327	$0.50-3.00
Flexible Foams	2,222	
Rigid Foams	1,382	
Coatings	500	
Adhesives	206	
Sealants	146	
Elastomers	207	
Thermoplastic PU	104	
Binders	354	
RIM (Reaction Injection Molding)	132	
Spandex	74	

Sources: API 1998, USB 2001, CMR 2002g

Transesterification uses the addition of an alcohol such as methanol to break the triglyceride down into a glycerol molecule and the fatty acids (Figure 3-13). The fatty acids can then be modified and polymerized using epoxidation or hydroformylation. The transesterification of soy oil is used commercially to produce methyl soyate used in solvents and biodiesel, a renewable fuel.

The **epoxidation** of soy oil is a well established technology and epoxidized soy oil has been used in resins for a long time. In 2001, 115 million pounds of soy oil was used in polyurethane foams, binders, coatings, adhesives, and sealants [USB 2001]. It is also possible to hydroxylate epoxidized soy oil resulting in a secondary alcohol or polyol structure (Figure 3-13). This process has been recently introduced into the market for use in urethanes for foams and other applications. DOE is co-funding research to significantly improve these chemistries to lower the cost and to reduce environmental impacts.

Hydroformylation is used to add hydrogen and a formyl group to an alkene (carbon chain containing one or more double bonds). This is carried out with petrochemicals using rhodium or cobalt catalysts to add hydrogen and carbon monoxide at the double bond. Rhodium is a very expensive metal and a cost-effective process requires complete catalyst recovery. Cobalt is much less expensive but still must be separated from the product to achieve the desired performance characteristics. These constitute the main technical barriers to the hydroformylation of vegetable oils.

When the reaction is performed on petrochemicals such as ethylene and propylene, the products are volatile and can be easily distilled from the catalyst. Vegetable oils are non-volatile and require a novel process for the separation of the products and catalyst. DOE co-funded research is investigating different ways of enabling complete recovery of the catalyst from the vegetable oil intermediates [DOEOIT 2001].

The product of vegetable oil hydroformylation is a polyaldehyde that can be hydrogenated to a primary alcohol or converted to polycarboxylic acid or polyamine (see Figure 3-14). Both hydroformylation and epoxidation can be used to produce polyols for use in polyurethanes or even polyesters, but the primary alcohols produced through hydroformylation are more reactive than the secondary alcohols produced through epoxidation.

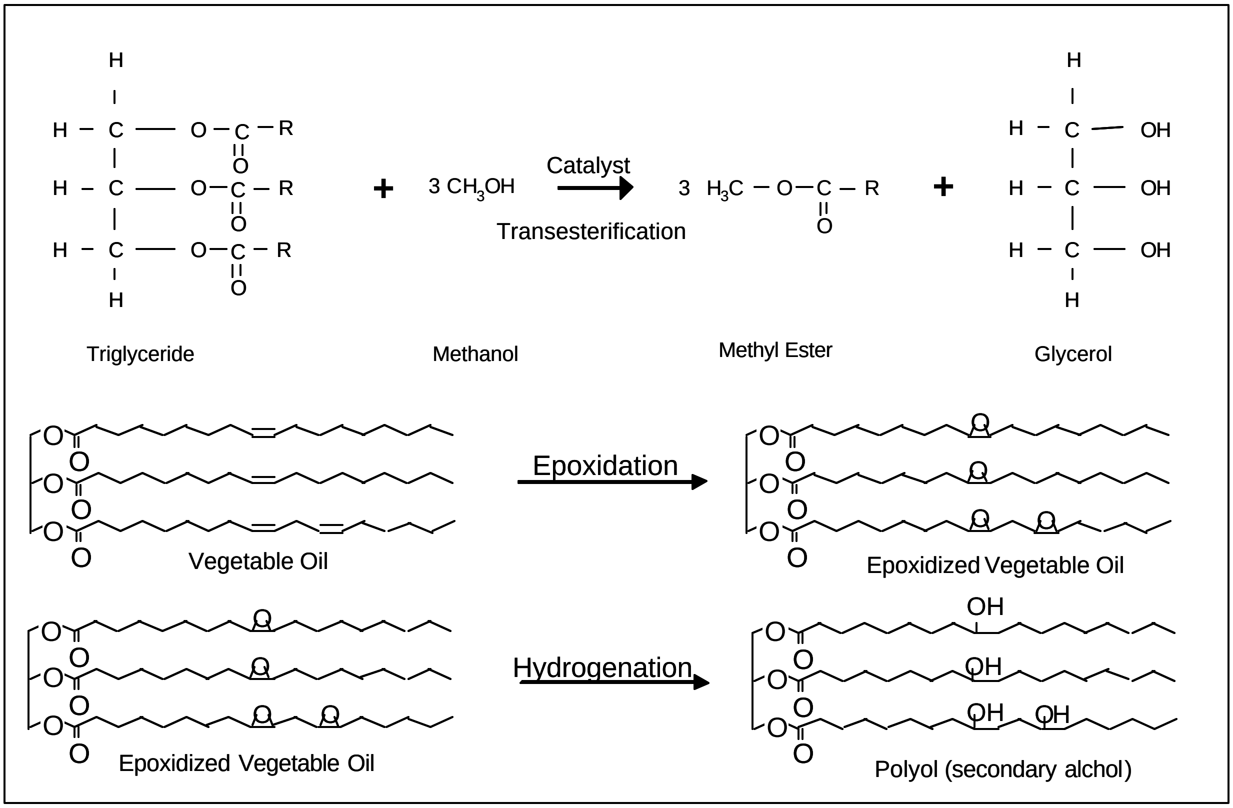

Figure 3-13 Transesterification and Epoxidation of Vegetable Oils

The increased reactivity opens up a variety of chemistries that can be used to create new polymers with novel properties. Vegetable oil-based polycarboxylic acids and polyamines are new materials whose properties may create additional inroads into the large polymer market. Research to effectively convert vegetable oil-based polyaldehyde to these materials is just now beginning to be pursued.

Metathesis is a reaction in which the carbon-carbon double bonds in an olefin (alkene) are cut and the "pieces" rearranged to yield new molecules (Figure 3-15). It is used industrially to convert nonpolar, unsaturated hydrocarbons such as 1,5-pentadiene and cyclopentadiene (ring-opening metathesis polymerization) using heterogeneous catalysts.

For materials containing polar functional groups such as those found in vegetable oils, the catalyst is very short-lived, making the process uneconomical. This might be overcome using homogeneous catalysis with catalyst ligand improvement and raw material purification. DOE has recently co-funded research in metathesis chemistry of vegetable oils. One of the goals is to use metathesis to convert fatty acid methyl esters to higher-value components.

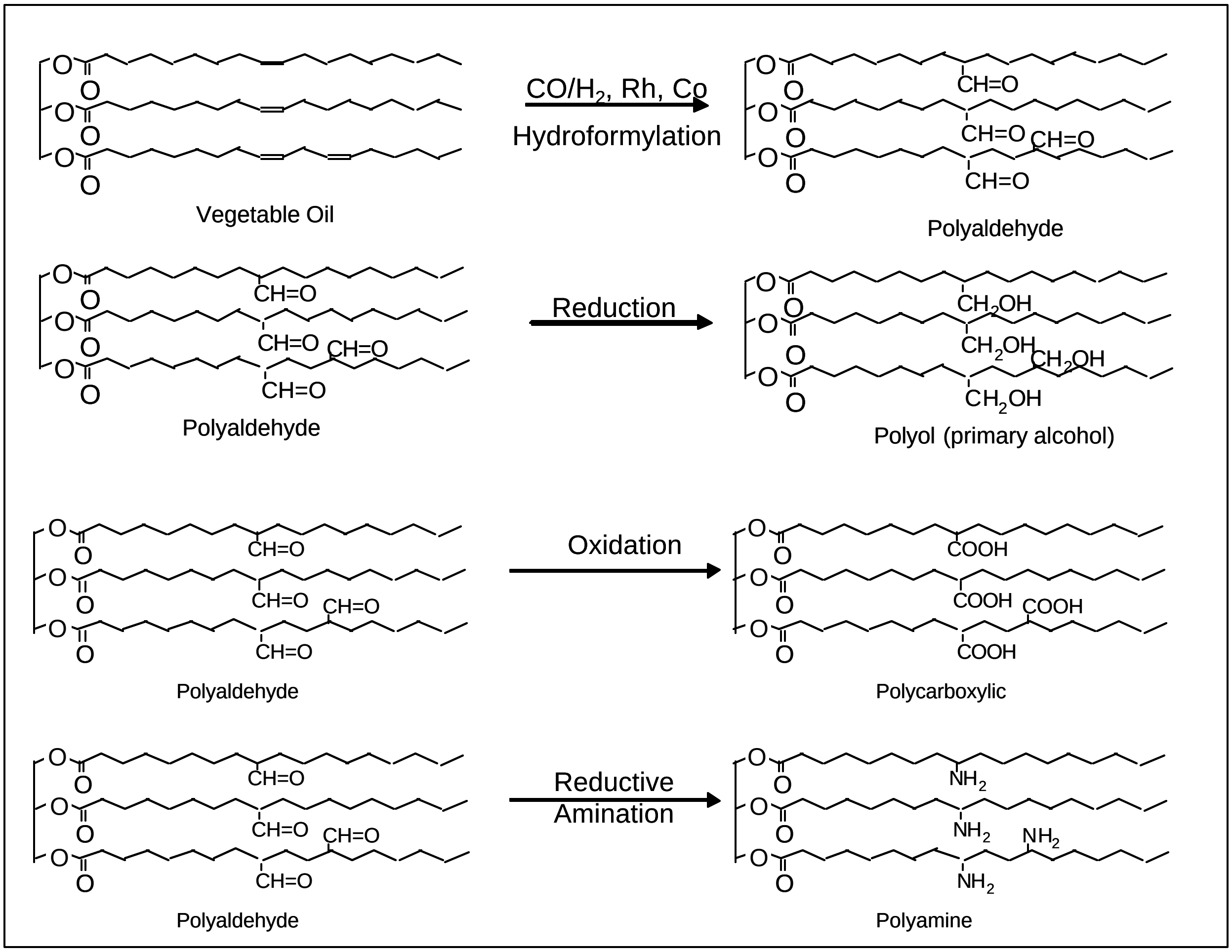

Figure 3-14 Hydroformylation and Subsequent Chemistries

Metathesis chemistry of vegetable oils can open up new opportunities for the use of vegetable oils in biobased products. It is a means to crack long chain fatty acids to medium length molecules while resulting in a terminal double bond. The terminal double bond could be reactive for free radical polymerizations or used to react and attach other functionality. It also provides the means to crack biobased fatty acids to medium length molecules very similar to costly synthetic lubricants produced from petroleum feedstock.

The outlook is very promising for vegetable oil-based polymer materials. The chemistries and applications are endless and researchers are just beginning to scratch the surface of potential opportunities

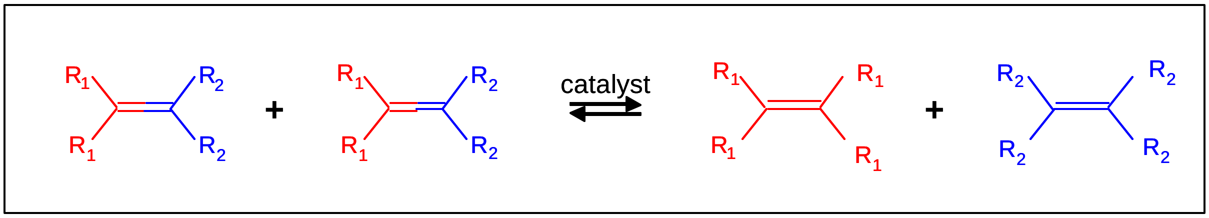

Figure 3-15 Generic Metathesis Reaction [UM 1995-1996]

Vegetable Oil Adhesives

Adhesives are nonmetallic substances, usually polymers, used to bond materials through adhesion and cohesion [Benedek 1997]. They are used in a range of industries including the electronics, automotive, construction, packaging, and medical sectors. Over 6 billion pounds (dry) of adhesives are used annually in the U.S. [ASI 2000]. Figure 3-16 depicts the current markets by adhesive delivery method.

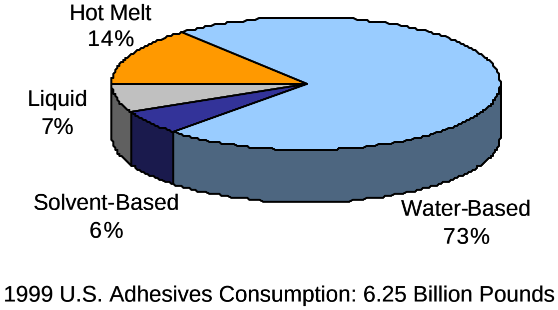

Figure 3-16 1999 U.S. Adhesives Consumption [ASI 2000]

Any polymer can serve as an adhesive. Thermoplastic or thermoset polymers can be used in water- and solvent-based adhesives. Water-born adhesives are also referred to as emulsion polymers. Liquid adhesives are chemically-reactive compounds such as epoxies, cyanoacrylates, silicones, and some phenolics. Hot melt adhesives consist of thermoplastic polymers that are applied as hot liquids to the materials to be joined and as they cool, they solidify to form a physical bond.

Most adhesives are petroleum-based polymers and in the past few years have been affected by high feedstock prices that cut into profit margins. As a polymer, vegetable oils can serve as the basis for many adhesives, offering a potentially lower cost alternative.

Vegetable oils can be chemically modified to contain functional groups capable of forming polar attractions with any surface. Numerous polar functional groups can be added, creating the potential for many different adhesive formulations. The addition of functional and reactive groups is enabled by the presence of double bonds in unsaturated fatty acids.

Adhesives can also be classified as structural, pressure sensitive, thermoplastic, pseudothermoplastic, and other, designations which crosscut adhesive delivery methods. Pressure sensitive adhesives (PSAs) show early promise as biobased alternatives. Approximately 600 million pounds of PSAs are produced each year and used in applications such as tape, sticky labels, diaper tapes, and medical products (transdermal drug patches, assembled disposable syringes, and tissue bandages) [ASI 2000].

The PSA market includes both rubber- and acrylic-based adhesives. Products in both groups can be water-based, solvent-based, or hot melt adhesives. Vegetable oils show promise for use in acrylic-based PSAs and are being explored by researchers at the University of Delaware [DOEOIT 2002a].

Surfactants

Surfactants are perhaps the most widely applied group of compounds in the chemical industry. They are the active ingredients in soaps and detergents, and are also important in the stabilization of emulsions (polymer production, etc), fabric softening, oil well drilling, and many other applications.

Vegetable oils have long been a source of fatty acids for detergents and soaps, but they compete with petroleum-based surfactants such as linear alkylbenzene sulfonates (LAS). In 1988, the U.S. produced 7.3 billion pounds of surfactants, of which approximately 12% was biobased [Chenier 1992, ICP 1994]. The fatty acids primarily consumed are medium-length chains such as lauric acid found in coconut oil and palm kernel oil. These oils are produced in countries such as Indonesia and imported into the U.S. for processing and use. In the early 1990s, approximately 1 billion pounds of medium chain-length fatty acids derived from coconut and palm kernel oil were imported annually [ICP 1994].

Today, new chemistries, crops and technologies are enabling the production of surfactants from domestic crops. Methyl ester sulfonate (MES) represents an opportunity for growth in vegetable oil-based surfactants. MES is an anionic surfactant derived from methyl esters and new reactor technology is said to remove major blocks to its use in detergent formulations as an alternative to LAS [CMR 2002a]. A plant with 164 million pounds of MES capacity was brought online late last year by Huish Detergents Inc. in Houston, Texas [CMR 2002a].

Methyl esters can be derived from lauric acid as well as fatty acids found in soy and other oils. Biodiesel made from soy oil, for example, is a type of methyl ester, which demonstrates that the technologies needed to perform this type of chemistry on vegetable oils are already available.

Oilseed crops have also been explored for use in surfactants. Species of *Cuphea* are a rich source of medium chain-length fatty acids such as those currently imported from Indonesia, including caprylic, capric, lauric, and myristic acid [ICP 1994]. Cuphea is attractive because it can be rotated with corn and soybeans every three years and helps to disrupt the life cycle of corn rootworms. Corn rootworms are responsible for more pesticide use on U.S. row crops than any other insect, and cost up to $1 billion annually in control and yield losses [ARM 1999].

Niche Markets for Oils and Lipids

Plant-based substances have long been used in niche markets such as the cosmetics and personal care industries. Oils such as sweet almond oil, apricot kernel (persic), avocado, borage, black currant seed, cherry kernel, coconut, cottonseed, evening primrose, flaxseed, grapeseed, ground nut (Arachis), hazelnut, hempseed, jojoba, and macadamia nut were used for their fragrance or moisturizing properties. The use of these oils has been small and little improvement to the purified oils has been pursued.

A combination of increased environmental awareness and the search for anti-aging products have spurred consumers to seek products whose main ingredients are “natural” rather than chemicals produced by the chemical industry. This has created a demand for personal care products containing moisturizers, antioxidants, and other substances derived from vegetable oil and other biomaterials. The domestic cosmetics market alone is valued at $27.1 billion. Pharmaceutical manufacturers are also exploring the greater use of plant-based derivatives in their products [AgV 1998, ARM 1997].

Some of these new products are a reinvention of established raw materials such as soy oil. ARS researchers have patented a route to a soy oil derivative that can be used in sunscreens [Compton 2002]. Additional patents have been filed on the conversion of ricinoleic acid to 7,10,12-trihydroxy-8(e)-octadecenoic acid and its derivatives for use as antifungal agents [Kuo 2001]. The conversion is done biochemically by *Pseudomonas aeruginosa*, a common bacterium. Less work has been done on the biochemical conversion of lipids than thermochemical methods and there are many potential discoveries on the horizon.

A newly established crop is meadowfoam, an oilseed that produces a light, high-quality oil with excellent moisturizing properties. It is prized by the cosmetics industry and is also a suitable high-grade machine oil [NPP 1999]. Meadowfoam is mainly grown in Oregon as an alternative crop by grass-seed farmers who are no longer allowed to burn their fields when switching from one grass seed to another. Instead of letting the field lie fallow and burning old seed, they can grow meadowfoam. The herbicides used in meadowfoam cultivation also get rid of old seed sprouts. Yields are about 1,000 pounds per acre with an oil content of 30%, and farmers earn between $100 and $700 per acre.

3.3.5 Protein-Based Bioproducts

Proteins are some of the most complex and unique polymers in nature. The functional properties of protein depend on its structure and advances in biotechnology hold promise for a variety of new protein-based materials. Two proteins that have long impressed scientists with their material properties are spider silk and marine adhesives. Spider silk has been estimated to be at least five times stronger than steel and twice as elastic as nylon, in addition to being waterproof and stretchable. Scientists in Canada have successfully modified goats to produce spider silk in their milk.

In general, very little has been done to explore proteins as industrial bioproducts, but the possibilities abound. The use of additives and simple chemical modification has shown the usefulness of protein in wood adhesives. A two-part adhesive system composed of soy protein hydrolyzate and phenol-resorcinol-formaldehyde (PRF) can be used to bond finger-jointed wood to form lumber. The advantages of the soy-PRF system over the conventional 100% PRF system include: 1) the ability to bond wet, frozen, as well as dried wood, 2) curing that proceeds faster and does not require heat or radiation; and 3) wood products that are straighter and more durable [USB 2000].

Work being performed at Kansas State University is more fundamental and is creating chemistries to enhance the structural properties of proteins for adhesives. The increased understanding of protein structure and function developed in this work could also be leveraged by researchers exploring other uses for proteins [DOEOIT 2002a].

Vegetable proteins are currently utilized in several other market sectors such as polymers, coatings, composites, inks, cosmetics, and personal care. However, their use is small leaving much room for the development of new, modified proteins with enhanced properties.

3.3.6 Bioproducts via Gasification

Gasification is the use of high temperatures and oxygen to transform solid carbonaceous material into a mixture of mostly gas and a small amount of liquid for use as fuels, chemical feedstocks, and power. Used since the early 1800s to gasify coal, the application of the technology to biomass has been studied extensively since the 1970s. It is now a matter of economics to commercialize biomass gasification systems. If oil prices increase and/or improved technologies significantly reduce costs, biomass gasification will be commercially viable.

The gas produced through gasification is synthetic gas (syn gas), a mixture of carbon monoxide (CO), carbon dioxide (CO_2), hydrogen, and methane. Syn gas can serve as a fuel to produce power and/or it may serve as one source of hydrogen for hydrogen fuel cells. Syn gas can also be converted to valuable chemicals and fuel.

Current methanol production is based on syn gas derived from natural gas, naphtha, or refinery light gas. Nearly 12.2 billion pounds of methanol are produced annually in the U.S. and while some is used as is, most of the methanol is converted into higher value chemicals such as formaldehyde (37%), methyl tertiary butyl ether (28%), and acetic acid (8%) [ACC 2000, CNI 2002]. An increase in natural gas prices may encourage the development of alternative processes such as biomass gasification to syn gas and subsequent conversion to methanol.

Ethanol can also be produced from syn gas. Research is being conducted in this area and biobased ethanol via syn gas could be as cost-effective as the sugars fermentation route.

Fischer-Tropsch chemistry is another approach for converting syn gas to valuable chemicals and fuels. The chemicals that can be produced include paraffins, monoolefins, aromatics, alcohols, aldehydes, ketones, and fatty acids (Table 3-21). These molecules can contain from 1 to 35 carbons. Fischer-Tropsch chemistry utilizes either cobalt (fixed-bed) or iron (fixed- and fluid-bed) catalysts with high temperature and pressure to convert the syn gas to chemicals and fuels. Yield, catalyst selectivity, and product composition depend on the catalyst, reaction conditions, and reactor type [Mangold 1982]. The process is highly exothermic and the principal problem in designing the reactor is heat removal.

A schematic of the Fischer-Tropsch (F-T) process with product composition is shown in Figure 3-18. The lighter hydrocarbons, C_1 and C_2, can be used to generate the hydrogen used downstream to refine the heavier hydrocarbons. In the future, the hydrogen may instead be recovered and purified for use as a transportation fuel. The alcohols can be recovered, purified, and sold without further processing. The rest of the product stream is subjected to fractionation and processing to recover and upgrade the various products.

The United States currently lacks the economic incentives to switch from petroleum to biomass gasification for the production of fuels and chemicals. However, in the near future some gas-to-liquid plants will be built at petroleum operations to use the excess natural gas that is currently flared. A few such plants are being considered by major petroleum companies [CMR 2003].

Other technologies utilizing syn gas include the biological conversion of syn gas to acetic acid or methanol. The DOE Industrial Technologies Program is supporting a project to convert reformed natural gas to acetic acid [DOEOIT 2002]. This route, which requires less energy than the thermochemical process, would have to produce acetic acid with a selling price between $0.42 and $0.46 to be cost-competitive with the current petroleum-based route [CMR 2002d].

Researchers at Southern Illinois University are investigating the potential of converting carbon dioxide to methanol using enzymes suspended in sol-gel [SIUC 2000]. Formation of formaldehyde, another valuable chemical, is an intermediate step of the metabolic pathway. Bench-scale feasibility tests have been performed and the next step will be to scale-up the process. This could serve as another avenue from gasification products to industrial chemicals.

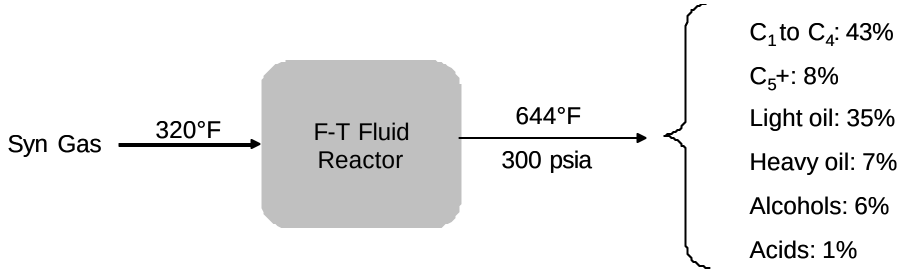

Figure 3-18 Example of Fischer-Tropsch Product Stream Composition [Mangold 1982]

Table 3-21 Potential Fischer-Tropsch Products From Syn Gas

Product	Current Applications	Market (M lb)	Price ($/lb)
Methane (SNG)	Uses: heating fuel, fuel gas (electricity/steam generation) Derivatives: multiple	7×10^{10} (18,986,745 Mcf)	$0.11-0.19
Propane	Uses: Aerosol propellant, fuel gas, refrigerant, process solvent Derivatives: ethylene, propylene, and others	397 (93.6 M gal)	$0.06-0.12
Butane	Process solvent Derivatives: 1,4-butanediol, maleic anhydride, acetic acid, acetone, acetylene, n-butyric acid, formic acid, isobutene, methyl formate, propionic acid	15,654[1] (3,242 M gal)	$0.15
Methanol	Uses: solvent Derivatives: formaldehyde, methyl tertiary butyl ether, acetic acid, other chemicals	12,180	$0.08-0.11
Ethanol	Fuel, solvent	11,682	$.012-.018
Isobutanol	Use: extraction agent Derivatives: multiple	116r	$0.30-0.50
Dimethyl ether	Aerosols	10-80	~$1.00-25.00
Methyl acetate	Derivatives: multiple	645	$0.60>
Dimethyl carbonate	Methylation/phosgenation reagent, oxygenate	95>	>$0.74
Gasoline	Fuel	804,043 (127,416 M gal)	$0.10-0.19[2]
Diesel	Fuel	393,634 (56,638 M gal)	$0.09-0.14[2]
Paraffin waxes	Barrier/antiblocking/heat sealing agent (hot melt adhesives), casting wax, electrical insulation, floor/shoe/car polish, plastics processing lubricant, rubber compounding	666	$0.23-0.25

[1] Includes natural gas plant production and refinery net production of finished petroleum products.
[2] Excludes taxes.

Sources: ACC 2000, EIA 2002, EIA 2002a, EIA 2001, CNI 2002, Ashford 2001, CRCDP 2002, CEH 2002, EIA 2001a, RFA 2002, EIA 2000a, OD 2000

3.3.7 Bioproducts via Pyrolysis

Pyrolysis is the direct thermal decomposition of the organic components in biomass in the absence of oxygen to an array of useful products such as liquid and solid derivatives and fuel gases [Klass 1998]. It is similar to gasification except that the mixture produced by the high temperature and pressure conditions consists mostly of liquid with some gas and solids. The gas could be used for its fuel value to produce power. The solids are very similar to powdered coal. The liquid could be used as a fuel to replace petroleum in applications such as home or commercial heating. Depending on pyrolysis conditions and feedstock, the liquid could also contain many valuable chemicals and chemical intermediates. The technical challenge is developing separation technologies capable of cost-effectively isolating these chemicals.

The technology closest to commercialization is the pyrolysis of high lignin-containing lignocellulosics which yields a replacement for phenol in phenol-formaldehyde resins (Table 3-22). Phenol-formaldehyde resins are used in plywood, oriented strand board (OSB), and many other applications. DOE co-funded research has shown that phenolic material from pyrolysis of wood bark and wood wastes can replace up to 50% of the phenol. Phenol-formaldehyde resins sell at $0.43-0.45 per pound [58]. Initial cost estimates suggest that pyrolysis of bark and other wood wastes could compete favorably in this market.

Table 3-22 Potential Markets for Lignin Derivatives

Chemical	Applications[1]	Current Market[2] (M lb)	Market Price[3] ($/lb)	Potential 2020 Market Size[4] (M lb)
Phenol-Formaldehyde	Plywood, oriented strand board, other wood composites	3,900	$0.30	Significant

[1] These are the applications targeted by the biobased chemical; some are current applications, others are new opportunities.
[2] This is the volume of market opportunities represented by the applications in the second column.
[3] This is the price of the current applications targeted by the biobased product and not the price of the biobased product.
[4] Authors' estimates of the biobased market in 2020 based on the state of the technology development and current U.S. applications market size.

Sources: APC 2000, CEH 2002

3.3.8 Biocomposites

Composites are composed of strong load-carrying materials with reinforcement embedded in a weaker material referred to as the matrix. The reinforcement provides strength and rigidity, helping to support the structural load. The matrix, or binder, maintains the position and orientation of the reinforcement, balances the load between the reinforcements, protects the reinforcement from environmental degradation, and gives shape and form to the structure.

Composites are a healthy and growing industry and scientists are continually developing new combinations of substances in search of stronger, lighter materials that perform better than those used today. Some of the older composites include steel-reinforced concrete, plaster casts, and wire-reinforced tires. More advanced materials use fiberglass, carbon fiber, and Kevlar as the reinforcement and polymer resins as the binder. Most of the binders are thermoset polymers (epoxies) with some thermoplastics (polyesters, polyamides).

Over the past few decades, high performance composites have replaced metals in some applications, and wood in many applications.

Biobased materials have the potential to replace one or both parts of a composite system while maintaining or improving performance. One simple example of a biobased composite is a moldable board material being developed by the USDA Forest Service Laboratory. The material consists of as much as 70-80% wood flour and the rest is a conventional plastic.

Automakers are increasingly looking to reduce the weight of their vehicles to help improve fuel economy and other performance characteristics. Ford has recently begun to use a polypropylene and kenaf fiber composite in the interior door panels of several of their cars [CSM 2000]. Plant fibers are very ductile and do not splinter, producing panels that are more shatter resistant than traditional composites made with wood flour or saw dust. They also weigh considerably less than traditional composites as well as the metal panels used in older cars.

The John Deere Company is using a composite that replaces conventional binders with a soy oil-based resin on some of its tractors. The composite panel could be 100% biobased if the fiberglass was replaced with natural fibers. In addition to kenaf, fibers that could be used include jute, sisal, coir, flax, and straw (wheat, rice). Natural fiber prices range from $0.03 per pound for jute to $0.25 per pound for kenaf compared to glass fibers which cost $0.50-0.75 per pound (carbon and Kevlar fibers are considerably more expensive). However, when the natural fibers are woven into mats or sheets, the price rises to $1.00-1.50 per pound [CSM 2000].

With the rapid advancements in biotechnology, materials science, and related fields, the potential for biocomposites is large. An example is a new, novel composite developed by the Affordable Composites from Renewable Sources (ACRES) group at the University of Delaware that has been demonstrated to be more conductive than silicon. Composed of a mixture of chicken feathers and a soy-based resin, it is hypothesized that the high air content of the feathers reduces the resistance and signals move twice as fast as they do in silicon chips [WashPost 2002].

3.3.9 Plants as Factories

In addition to being processed and converted into sugars or other components for industrial products, plants can also produce bioproducts directly within their tissue. Lumber, paper, and cotton fiber are examples, though they are not a focus of this report. Starch used almost directly from corn grain in paper coatings and other industrial products is another example. Antioxidants such as vitamin E and other tocopherols are produced naturally by certain plants and can be extracted and purified for use in health care products.

Researchers at Archer Daniels Midland are looking at the feasibility of extracting valuable tocopherols and sterols from corn fiber and then using the sugars in the fiber as feedstock for renewable chemicals and fuels in a biorefinery. Tocopherols and sterols can be worth several dollars per pound and with the increase in health awareness, demand for such health care substances is increasing.

These examples are at the two ends of the spectrum in terms of the potential value of *Plants as Factories*. Through advances in separation technology and genetic modification of plants, there could be many cases where plants directly produce a final product or at least an intermediate that requires fewer processing steps to reach the final product. Examples with this potential are shown in Table 3-23.

Polyhydroxyalkanoates (PHAs) are a polymer family with great potential for commercial success. PHAs are polyesters produced naturally by many bacterial species for carbon and energy storage. They can be produced through fermentation (see Section 3.3.1), but a more cost-effective approach is to genetically modify a plant to produce PHAs directly within the plant.

DOE is co-funding a project to produce PHAs in switchgrass which can then be extracted from the plant material and processed to obtain a consistent composition and the desired material properties. The plant material remaining after PHA extraction can be used to produce fuels, power, or other products, creating the opportunity for a “plants as factories” biorefinery. There are many types of PHAs each with their own properties and it is possible that in the future PHAs could figure prominently in the plastics market.

Guayule is another emerging bioproduct-producing plant that is being developed by the USDA, Yulex Corporation, and other organizations. It is a desert shrub indigenous to the southwest U.S. and northern Mexico and produces a **natural rubber latex** primarily in the cells of the bark. Natural rubber currently on the market comes from the Brazilian rubber tree (*Hevea brasiliensis*) and is commonly used in medical device components.

Natural rubber latex allergy has become an issue in the U.S. as approximately 20 million Americans are allergic to the proteins found in *Hevea* rubber [AFIHT 2001]. Guayule rubber is allergen free and the initial target applications include gloves, condoms, and other products where the strength and resiliency of natural rubber is desired without the potential allergic reaction.

Approximately 20,000-50,000 pounds of rubber can be produced per acre of guayule. The plant also contains a resin that shows promise as a coating for wood to protect it from termites and wood rot [ARM 2002a].

Another plant that has been identified as a potential *Plants as Factories* is **milkweed** The fiber is used as a filling in comforters and pillows, but it has been discovered by an ARS researcher that the leftover seedmeal can be used as an alternative to methyl bromide to control nematodes [ARM 1999]. The timing is opportune as studies by the World Meteorological Organization, National Oceanic and Atmospheric Administration, and National Aeronautics and Space Administration indicate that methyl bromide contributes to destruction of the ozone layer. In 1999, the U.S. Environmental Protection Agency began a phase-out of methyl bromide that is to be completed in 2005 [EPA 2002d]. The mandated methyl bromide phase-out will create an annual demand of approximately 55 million pounds for methyl bromide alternatives [USDA 2002b].

Another interesting application is vegetable oils. Some companies are considering the possibility of genetically modifying oil plants to produce more of a particular desired fatty acid, or even a new fatty acid with a structure more favorable for use in industrial products.

3.3.10 Less Explored Concepts: Photosynthetic Organisms and Anaerobic Digestion

There are feedstocks and technology options that could have significant promise for bioproducts, but have not yet been the focus of much research. Two of interest are photosynthetic organisms and anaerobic digestion.

Photosynthetic Organisms

Photosynthesis is the process by which plants combine sunlight with carbon dioxide and water to generate carbohydrates. Photosynthetic organisms have been considered for the production of fuels, chemicals, and hydrogen but to date very little research has been conducted in this area. One process used industrially is the photosynthetic production of the pink food coloring used to color salmon. The cost-effectiveness and scalability of photosynthetic systems is a major hurdle for commodity chemical production. As biotechnology advances, photosynthetic organisms may begin to play a role in the bioproducts industry.

Anaerobic Digestion

Anaerobic digestion is a process that utilizes anaerobic bacteria to produce methane and carbon dioxide gas from organic matter. It is currently used to reduce the organic matter in domestic, municipal, agricultural, and industrial wastes and wastewaters to a usable fuel gas referred to as biogas. The gas could also be upgraded to fuels and chemicals using Fischer-Tropsch chemistry (see Section 3.3.6).

Table 3-23 Plants as Factories

Product	Applications[1]	Market Size[2] (M lb)	Current Price[3] ($/lb)	Potential 2020 Market Size[4] (M lb)
Tocopherols/ Sterols	Vitamins, cholesterol-lowering products	7 (vitamin E)	$1.00-2.00	*
Guayule	Natural rubber applications	2,184	$0.25-0.59	*

Table 3-23 Plants as Factories

Product	Applications[1]	Market Size[2] (M lb)	Current Price[3] ($/lb)	Potential 2020 Market Size[4] (M lb)
PHAs	Thermoplastic polymer applications	30,000	$0.30-1.50	If technology is successful, could be >4,000
Milkweed	Fiberfill applications	2,769	$0.56	*
	Methyl bromide alternative	55	$4.00-5.00	*

*Not projected

[1] These are the applications targeted by the biobased chemical; some are current applications, others are new opportunities.
[2] This is the volume of market opportunities represented by the applications in the second column.
[3] This is the price of the current applications targeted by the biobased product and not the price of the biobased product.
[4] Authors' estimates of the biobased market in 2020 based on the state of the technology development and current U.S. applications market size.
Sources: ITA 2001, USDA 2002b, EPA 2001, ARM 1999, CEH 2002

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NOTE 1	Assumes energy content of 21,000 Btu/lb for biomass. Based on 2000 data for organic chemicals production from the American Chemistry Council, *Guide to the Business of Chemistry.*
NOTE 2	Assumes 5.9 million Btu/barrel of oil, 13,161 Btu/lb ethanol (higher heating value), and oil consumption associated with gasoline is about 7.9 million barrels/day or about 2.9 billion barrels/year. Assumes delivered prices of biomass residues at $50/ton, coupled with accelerated technology development.
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Appendix A

Major Biomass Feedstocks and Derivatives

Figure A-1 Bioproducts From Corn [Ashford 2001, CRA 2002]

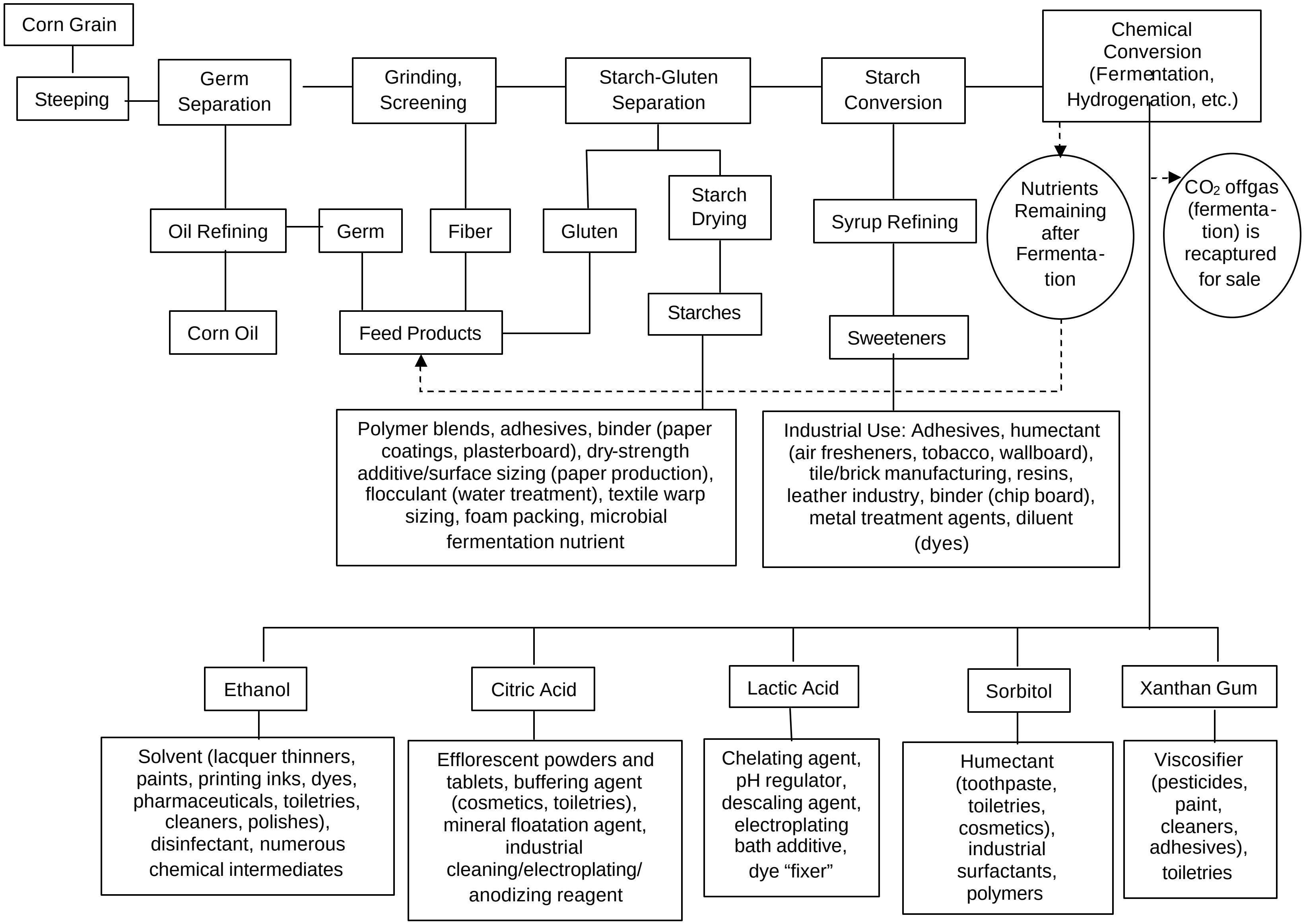


Figure A-2 Bioproducts From Soybeans [Ashford 2001]

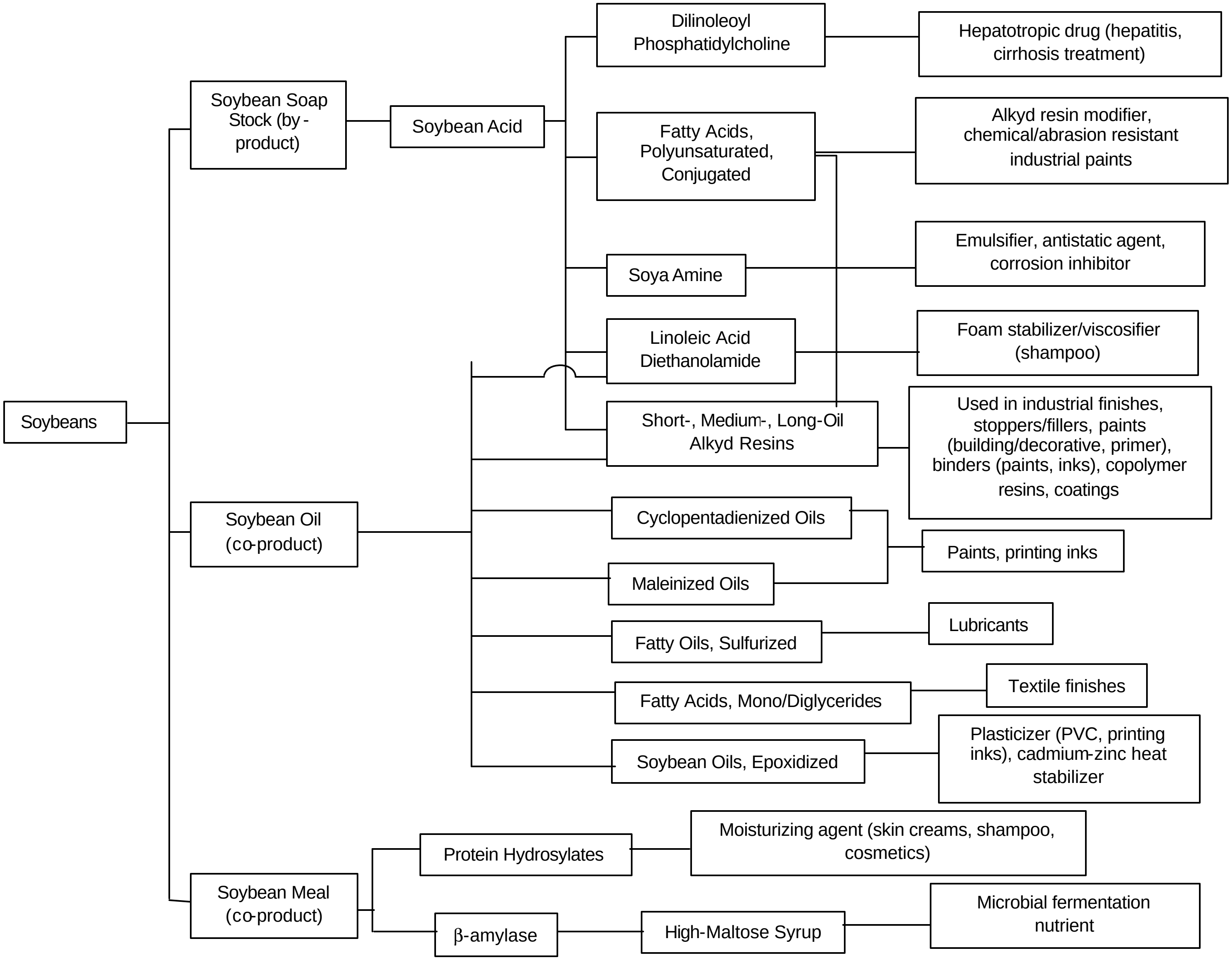
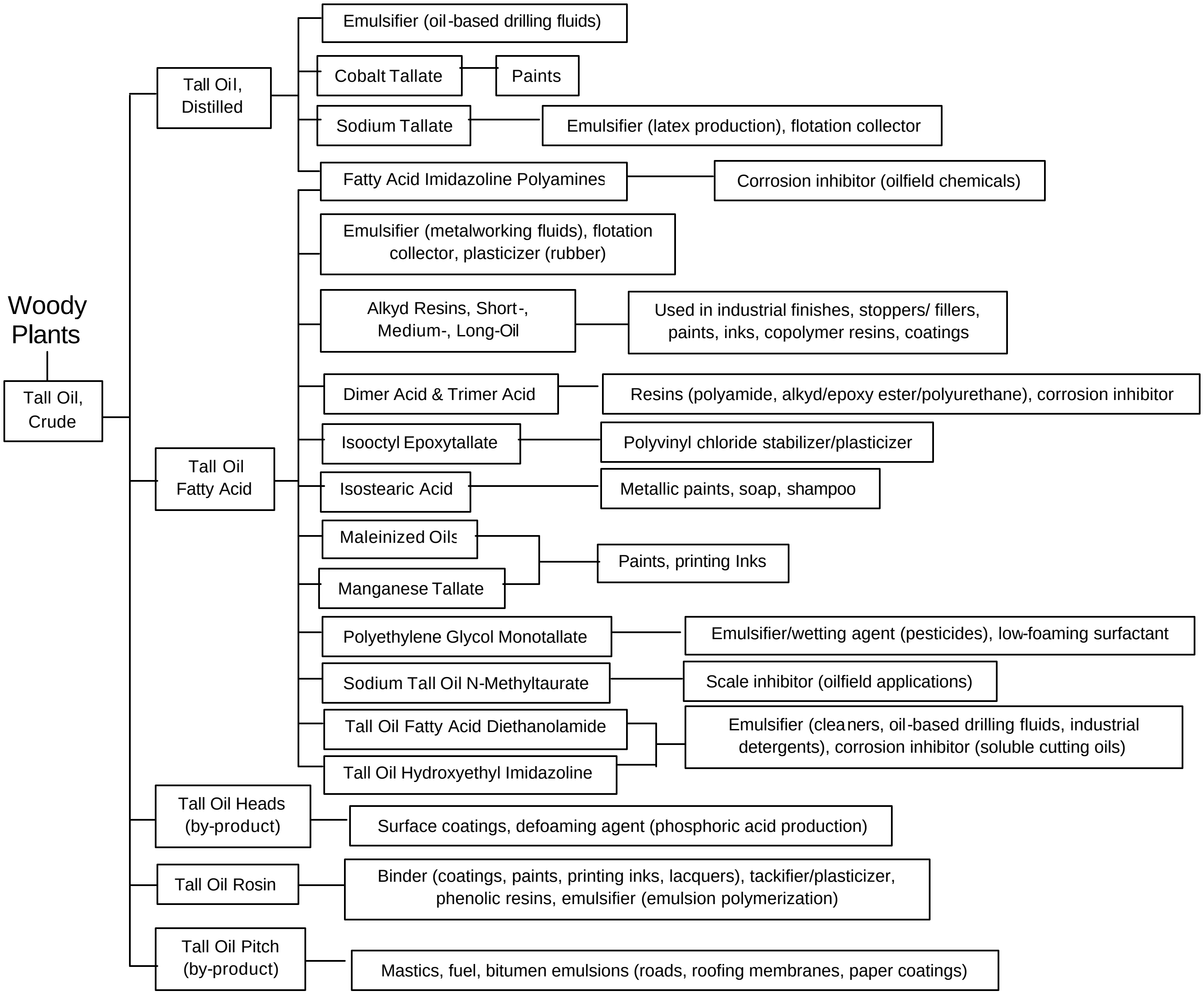


Figure A-3 Bioproducts From Tall Oil, A Wood-Derived Chemical [Ashford 2001]



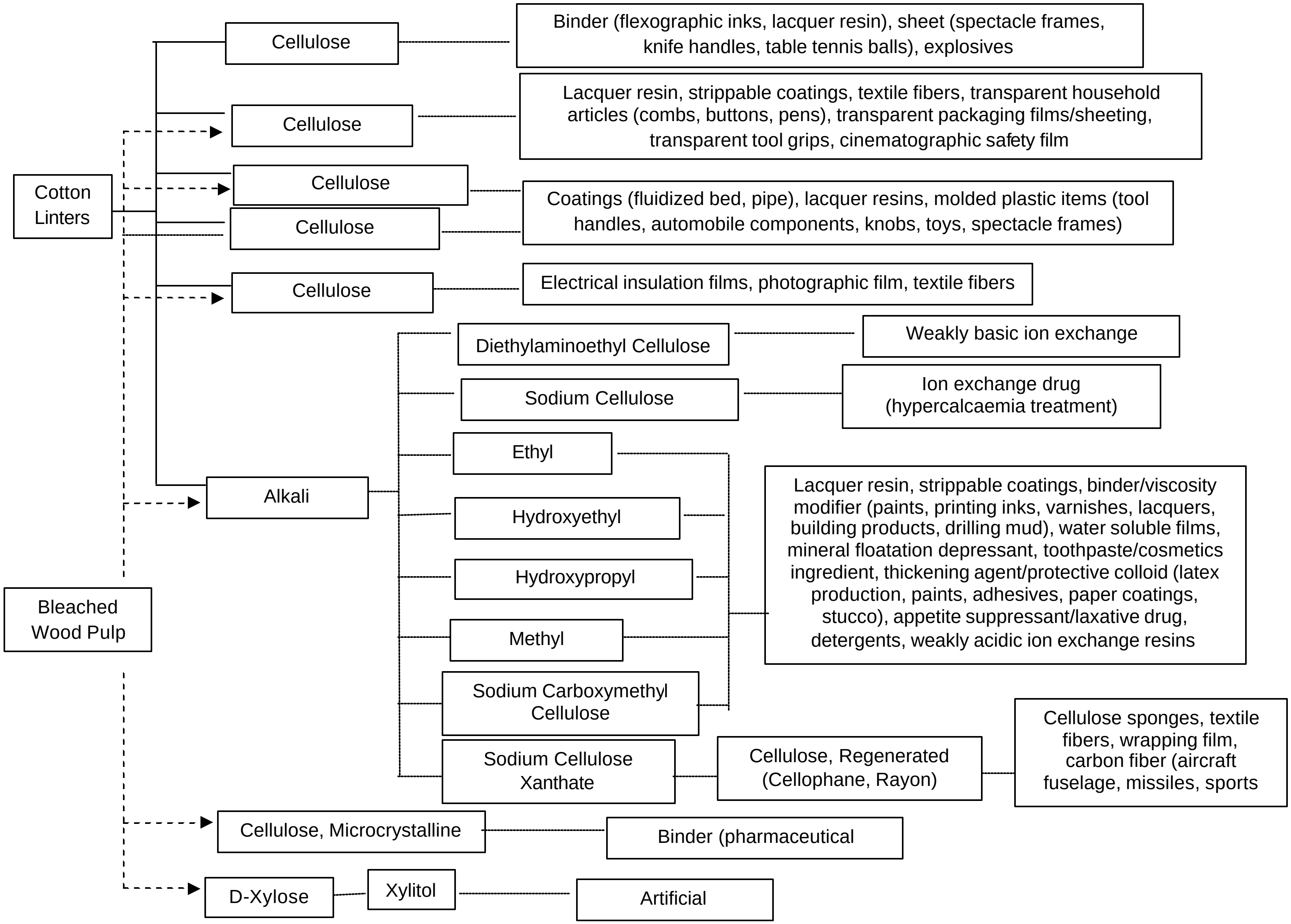


Figure A-4 Bioproducts From Cellulose [Ashford 2001]

Figure A-5 Bioproducts From Castor Oil [Ashford 2001]

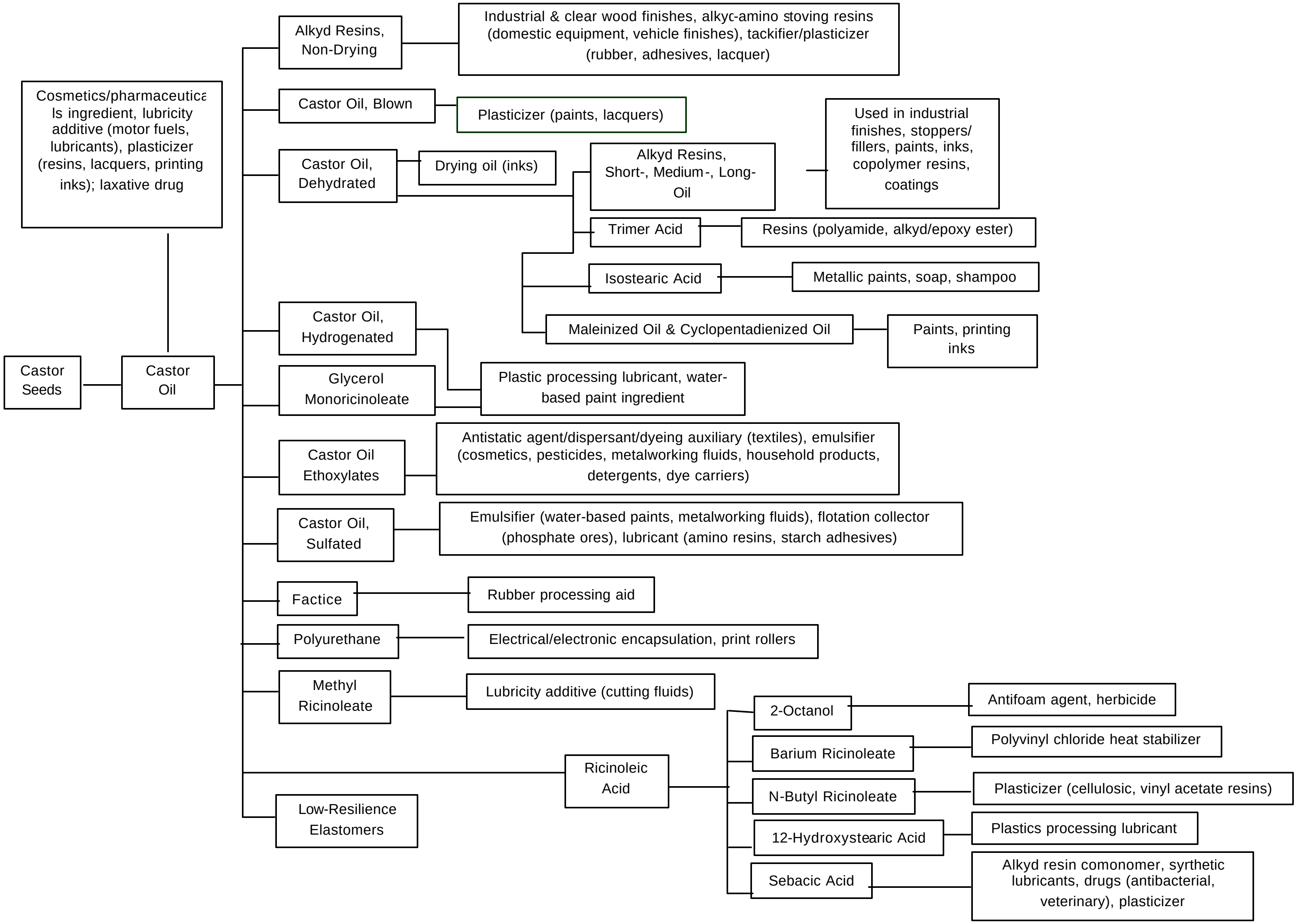
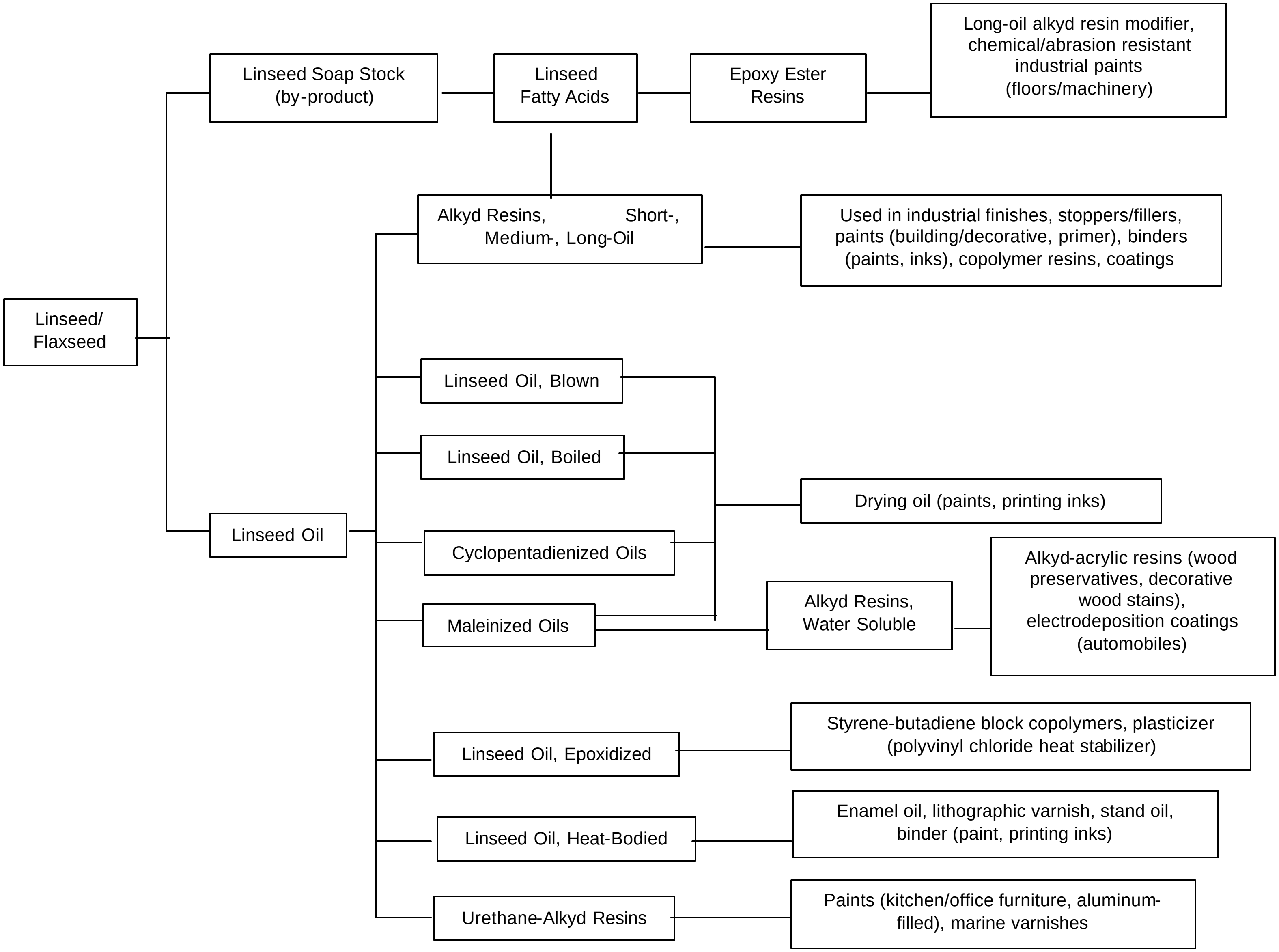


Figure A-6 Bioproducts From Linseed and Flaxseed Oils [Ashford 2001]



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