Value-added Coproducts from the Production of Cellulosic Ethanol

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Cellulose is a major constituent of plants and soon may become an important component in our mix of energy sources. Cellulosic ethanol is made from biomass, including wood, grasses, agricultural residues, and municipal solid waste. By producing ethanol, we can reduce our country's demand for petroleum, lower transportation costs, reduce greenhouse gas emissions, and provide more economic stability. The federal Energy Independence and Security Act of 2007 mandates that by 2022, the U.S. produce 36 billion gallons of biofuel per year, of which 16 billion gallons (nearly 10 percent of the total U.S. transportation fuel supply) must be cellulosic ethanol (1).

Corn stover in northern Colorado. Photo by Warren Gretz, 2001. Courtesy of DOE/NREL.

Importance of Coproducts

As with all new technologies, turning a potential energy source into a profitable one requires an economic analysis of each step. A market for coproducts improves the economic equation. As described in the *Annual Energy Outlook 2007* published by the U.S. Department of Energy, "The value of co-products will play a significant role in determining which crops are most profitable for farmers to grow, and biofuels producers to use" (2). High prices for coproducts support crop prices for agricultural producers while offsetting feedstock costs for ethanol producers. Manufacturing products other than fuels also allows for profits less dependent on oil prices. High-value coproducts, in some cases, could even become more valuable than the ethanol (3). Of the 300 potential products from biomass (4), about twenty are potential candidates as coproducts from cellulosic ethanol production (Table 1, page 6).

Methods of Ethanol Production

Biomass is made up of three major components: cellulose, hemicellulose, and lignin. Cellulose makes up 40 to 60 percent of the biomass by weight. This complex, tightly-bound sugar polymer is made of glucose, a C_6 sugar. Hemicellulose (20 to 40 percent of the biomass by weight) is composed of primarily pentose (C_5) sugars, including xylose, arabinose, mannose, and galactose, as well as glucose. The third component of biomass, lignin, is a complex polymer that provides strength to the cell walls. Lignin makes up 10 to 24 percent of the biomass by weight (5).

Due to the difficulty in separating these components, the production of ethanol from biomass is a complex and, until recently, expensive process. There are two basic ways to do this. In the **biochemical** method, the feedstock is pretreated to separate the hemicellulose from the cellulose and lignin (Figure 1, page 2; video link). The cellulose is treated by enzymatic or acid hydrolysis to break down the long-chain glucose units. Ethanol is then produced by the fermentation of these simple sugars by microbes, each specific to the type of feedstock (6, 7).

Ethanol fermentation tanks at the Biochemical Process Development Unit at the National Renewable Energy Laboratory's Alternative Fuels User Facility in Golden, CO. Photo by Pat Corkery, 2009. Courtesy of DOE/NREL.

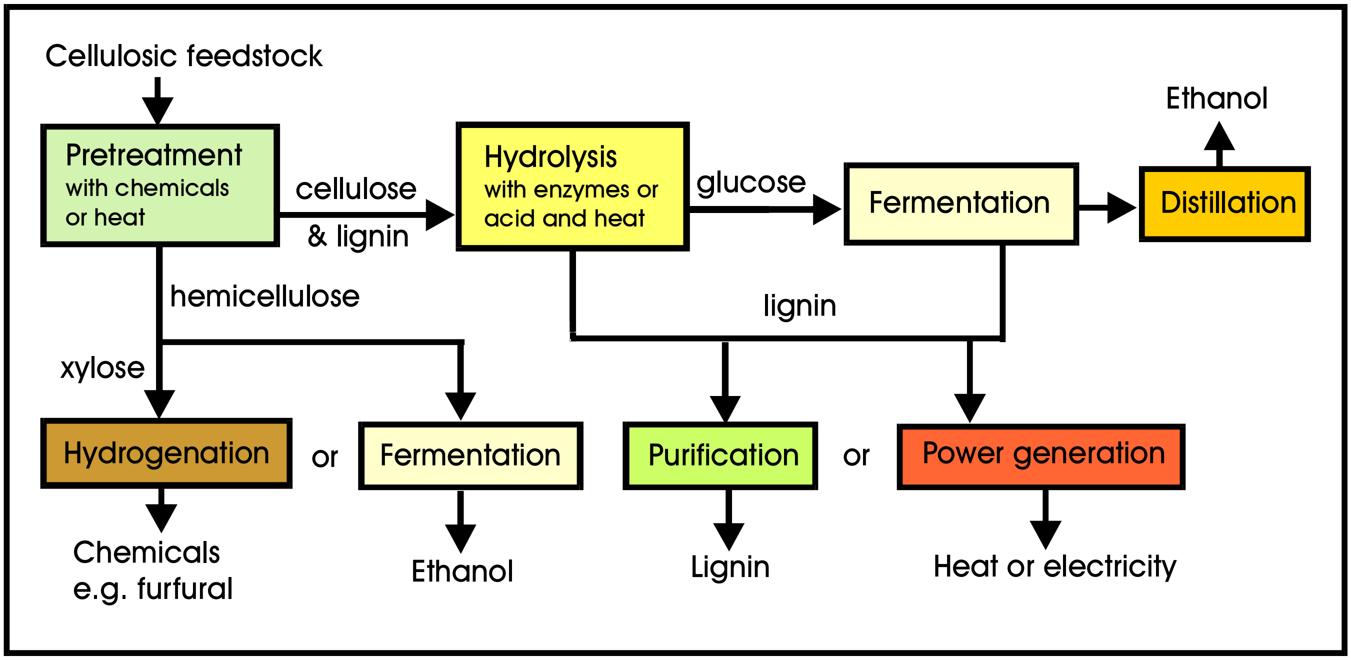

Figure 1. Biochemical production of cellulosic ethanol.

The **thermochemical** process uses heat to convert biomass into liquid fuels. This method is particularly suited for feedstocks high in lignin, such as wood. Partial combustion at low temperatures in the absence of oxygen produces **pyrolysis** oil that is then refined to liquid fuels (8) (Figure 2).

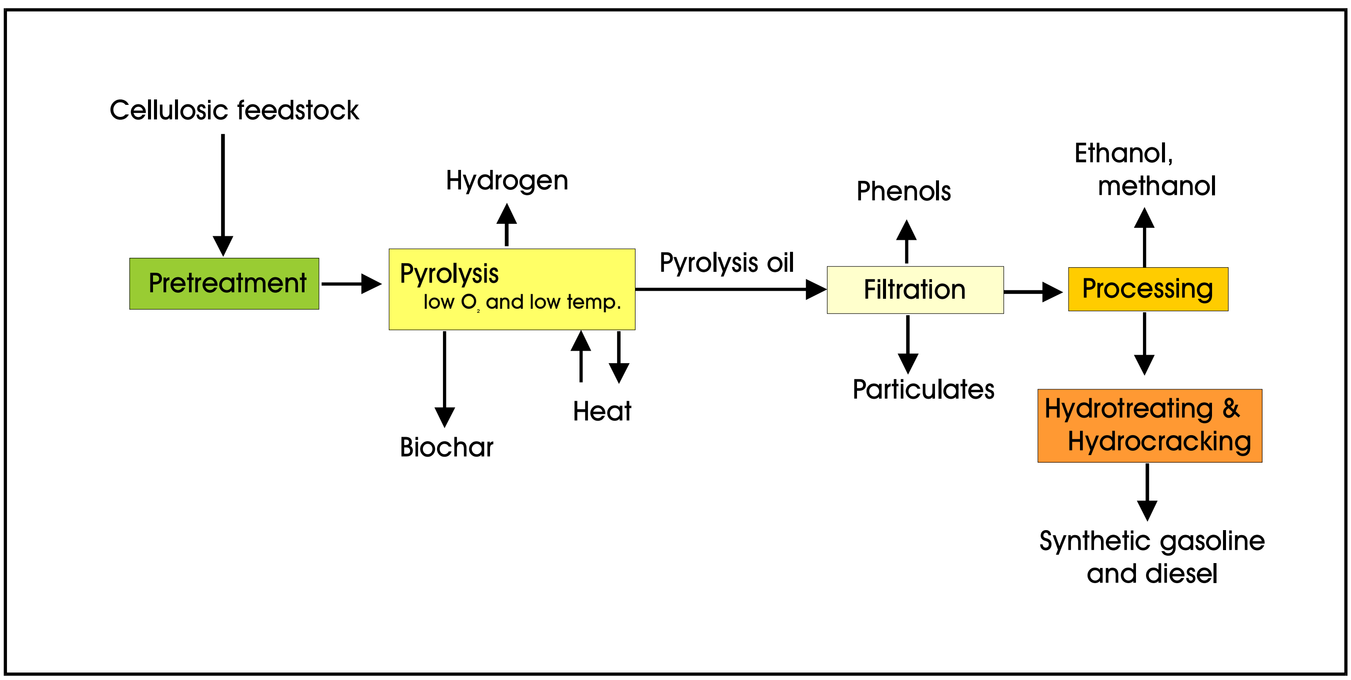

Figure 2. Thermochemical production of cellulosic ethanol using pyrolysis.

Another type of **thermochemical** conversion, **gasification**, also uses partial oxidation but at higher temperatures to create synthesis gas ("syngas", primarily CO and hydrogen), which is then converted into ethanol and other alcohols by fermentation or in a catalytic reactor (9, 10) (Figure 3 and photo, page 3; video link).

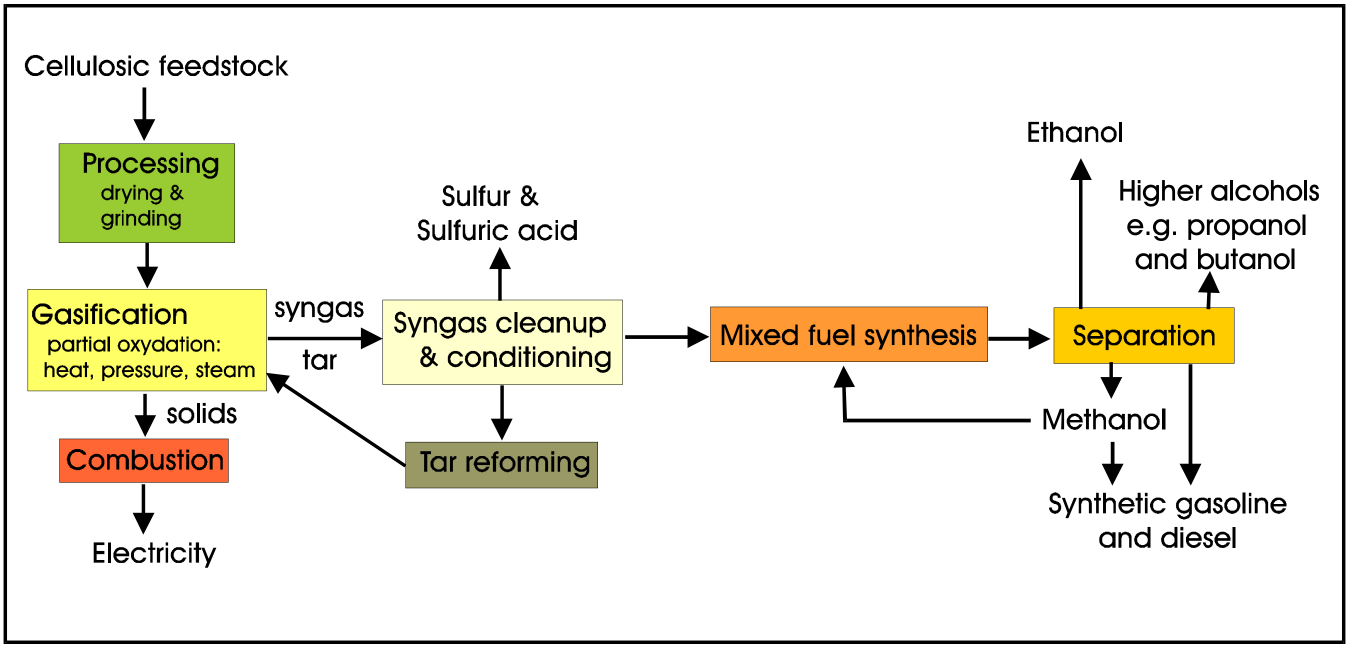

Figure 3. Thermochemical production of cellulosic ethanol using gasification.

Biorefineries

In order to test production methods with less investment risk, small pilot plants and somewhat larger demonstration plants are built before scaling up to commercial-size plants. Currently, in the case of cellulosic ethanol, several pilot and demonstration plants have been built with capacities generally less than one million gallons per year (Table 2, page 7). Commercial plants are planned that will have production capacities of 20 to 100 million gallons annually (11, 12). Total capital costs of a plant with an annual capacity of 50 million gallons are estimated to range from $176 million to $375 million, four to six times that of corn ethanol plants of the same size (2, 13). Some plants are designed for a single feedstock, while others emphasize their flexibility in utilizing various sources (14) (Table 2).

Integrated biorefineries are patterned after petrochemical refineries in that a variety of products may be produced at one location. Flexibility in the production of several low-volume coproducts based on current markets would provide an economic advantage (15, 16). However, the financial risk of introducing several coproducts at once may require the introduction of one product at the beginning, and phasing in others later (16). The goal is to make all products marketable.

Syngas is produced by the Thermochemical Process Development Unit at the National Renewable Energy Laboratory in Golden, CO. Photo by Warren Gretz, 2000. Courtesy of DOE/NREL.

Various methods of fuel production also may be combined in one plant. For example, lignin has an energy content similar to coal, and the lignin produced by an ethanol plant is often burned directly for heat or electrical generation. Another scenario is one used by ZeaChem, Inc.: the fermentation of glucose and xylose for ethanol and the gasification of lignin to produce hydrogen-rich syngas (17). Another type of integration is the co-firing of coal with biomass or lignin. This has proven successful at Alliant Energy Corporation's Ottumwa Generating Station in Iowa. Switchgrass is burned with coal, providing five percent of the energy requirement and reducing sulfur dioxide and particulate emissions (18). Co-firing is also planned at the Spiritwood Energy Park near Jamestown, North Dakota, where lignin produced by a proposed cellulosic ethanol plant (19) will be burned by Great River Energy's Spiritwood Station, a coal-fired plant. The power plant will then provide steam to the ethanol plant, thus increasing the efficiency of both (20).

Alliant Energy's Ottumwa Generating Station, a co-firing power plant in Iowa that burns coal and switchgrass. Photo by Wade Amos, 1999. Courtesy of DOE/NREL.

Coproducts from the Biochemical Process

In the biochemical production of ethanol (Figure 1), other materials from the process, such as hemicellulose, lignin, and proteins, as well as gases released during fermentation, can be used to make a wide variety of products (Table 1).

Xylose, a major component of hemicellulose, can be fermented by specific microbes to produce ethanol, but also may be processed to produce furfural, a solvent and feedstock for pesticides and resins (21); or xylitol, a sweetener (22). Sugars from the hemicellulose stream are also valuable as animal feed. Inbicon of Denmark produces ethanol and a C_5 sugar-based "molasses" from wheat straw (23).

The short-chain glucose not used to make ethanol may be used to produce organic acids, alcohols, and polymers (see Table 1). Some of these compounds are food additives and others are used in industry to produce a wide variety of products including solvents, detergents, textiles, and plastics, including a biodegradable plastic, PHA (24).

Succinic acid is one coproduct made from glucose that appears to be very promising, serving as a replacement for petroleum-derived maleic anhydride, which is important in the production of surfactants, solvents, detergents, plastics, fibers and pharmaceuticals (25, 26). It is predicted that the market for succinic acid would grow "substantially" if the current high price were to decrease (16).

The production of cellulose nanofibers in conjunction with ethanol production may also be profitable as reported by Leistritz *et al*. (27). Nanofibers (or "nanowhiskers") are made from non-hydrolyzed cellulose and are combined with resins to produce moldable, reinforced composites for the automotive, aerospace, and other industries (28, 29). Wheat straw appears to be the most promising feedstock for this material due to its high cellulose content as compared to other grasses (27).

A cellulosic ethanol plant produces as much as 27 lbs. of lignin for every 100 lbs. of feedstock (2). Using mild methods to separate lignin from the biomass early in the process will preserve its structure, allowing for more potential uses (30). Lignol Innovations uses wood and agricultural residues in their pilot plant in British Columbia to produce ethanol and high purity lignin (31). This form of lignin has large-scale commercial potential as a replacement for petroleum-based products currently used in the manufacturing of industrial coatings, gels, and emulsifiers (32).

Pretreatment process under study to hydrolyze hemicellulose and solubilize lignin at Golden, CO National Renewable Energy Laboratory. Photo by Warren Gretz, 2002. Courtesy of DOE/NREL.

Another important use for lignin is in the production of carbon fiber. Spun and woven into a fabric, carbon fiber is combined with resins to form reinforced plastic. This material is similar to fiberglass, with high tensile strength and low weight, and is used in aircraft, automobiles, and sporting goods (30).

Protein for animal feed may be removed from the biomass before the pretreatment process, as proposed by Abengoa Bioenergy (33). Late-season switchgrass and agricultural residues contain about three to six percent protein (6, 34). Bruce E. Dale of Michigan State University has developed a method using an alkaline treatment followed by membrane filtration to remove 60-80% of the leaf protein. The conversion from soybean and corn acreage to switchgrass production may be more acceptable if animal protein for livestock is also produced (35).

Coproducts of the Thermochemical Process

The thermochemical method of ethanol production (Figures 2 and 3) also produces other liquid fuels such as methanol, and with further treatment using the Fischer-Tropsch process, "synthetic" gasoline and diesel, butanol, and dimethyl ether, a propellant and liquid fuel of use in diesel engines.

Biochar is the solid residue from the process of pyrolysis (Figure 2) when using biomass or lignin. It can be burned like coal or used as a soil additive to improve soil structure and prevent the loss of nutrients and water. Biochar can also be used to sequester carbon and may remain in the soil for hundreds of years, mitigating the release of carbon into the atmosphere through the use of fossil fuels (36).

Other coproducts of either pyrolysis or gasification include olefins (alkenes: used in the production of polyethylene and other materials), and various higher alcohols. Hydrogen gas resulting from the gasification of biomass or lignin may in itself become an important fuel source as hydrogen fuel cells become more prevalent (18).

Switchgrass grown at the University of Alabama's test plot near Auburn, Alabama, with David Bransby. Photo by Warren Gretz, 1996. Courtesy of DOE/NREL.

The Future of Cellulosic Ethanol

New technology is expected to improve the current ethanol output of 50 gallons per ton of biomass to 80 to 135 gallons per ton (37, 38, 17). In the case of switchgrass, the development of improved strains may increase annual production to 12 tons per acre or more (37). This may result in the production of 960 to 1620 gallons of ethanol per acre, as compared to the current average of 400 gallons per acre of corn (39). Researchers have projected that production costs of cellulosic ethanol could go as low as $0.60 per gallon, equivalent to less than $1.00 per gallon of gasoline on an energy equivalent basis (40, 7).

The production of cellulosic ethanol will become more efficient and profitable with further improvements in feedstock and enzyme production, chemical treatments, plant energy efficiency, and the market for coproducts. With commercial plants coming on line in the next few years, we will soon realize the economic and environmental benefits of ethanol made from cellulose, the most abundant organic compound on Earth.

Table 1. Value-added coproducts from cellulosic ethanol production.[1]

Product	**Source**	**Process**	**Uses** (both the product and its derivatives) (Reference number)
Gases and fuels			
syngas	biomass or lignin alone	gasification	used to produce ethanol, methanol, dimethyl ether, olefins, mixed alcohols (propanol, butanol)
hydrogen	lignin	gasification	fuel cells, industrial uses (18)
carbon dioxide	sugars	fermentation	industrial uses
"synthetic" gasoline and diesel	pyrolytic lignin	hydrotreating/ hydrocracking	liquid fuels
lignin	lignin	---	fuel: combustion for heat and electricity
Organic acids			
succinic acid	glucose	fermentation in high CO_2	food additive, plastics, surfactants, detergents, solvents, textiles, pharmaceuticals (25, 26, 41)
lactic acid	glucose	fermentation	food and beverages, and converted to polylactic acid (PLA) used as a polymer and in textiles (41)
acetic acid	glucose	fermentation	food additive, and industrial chemical. Used in the production of polyethylene terephthalate (PETE; used in packaging, textiles, and films), ethyl acetate (a solvent), glues, and fibers
fumaric acid	glucose	fermentation	food additive, and used to produce resins and alcohols (25)
Alcohols			
n-butenol	glucose	fermentation	liquid fuel, food additive, solvent
xylitol	xylose	hydrogenation	sweetener (22)
Aromatic compounds			
furfural	xylose, arabinose	dehydration	solvents, pesticides, resins; converted to liquid fuels (21)
benzene, toluene, xylene	lignin	catalysis	solvents and intermediates for production of styrene (polymers and plastics), phenol (adhesives and resins), nylon (30)
Macromolecules			
cellulose nanofibers	cellulose	chemi-mechanical treatment, electrospinning	structural composites, plastics, films (27, 28, 29)
polyhydroxyalkanoate (PHA)	glucose	fermentation	biodegradable plastic used in films, packaging, fibers, coatings, foams, and in medical and pharmaceutical applications (24)
lignosulfonates[2]	lignin	sulfonation	dispersants, emulsifiers, binders, sequestrants, adhesives, fillers
carbon fiber	lignin	melt-spinning	reinforced plastics for vehicles (30)
high purity lignin	lignin		coatings, emulsifiers, gels, anti-oxidant and anti-microbial products, polymers (31, 32)
Other products			
pentose (C_5) sugars	hemicellulose	---	animal feed (e.g. "molasses") (23)
protein	protein	---	animal feed (33, 35)
biochar	lignin	combustion	fuel, soil additive, and used in carbon sequestration (36)

[1] Currently in production or those with high potential based on technical and economic feasibility.
[2] Currently byproducts in the production of wood pulp; most commonly added to concrete as plasticizers.

Table 2. Selected companies[1] producing cellulosic ethanol and coproducts (in production or development).

Company	**Location**	**Feedstock**	**Production capacity** (in million gallons/yr)	**Coproducts**[2] (and Reference)
Abengoa Bioenergy New Technologies	Spain Nebraska Kansas	agricultural residues and switchgrass	1.3 80 gal/day 15 (in 2012)	lignin, protein (33)
California Ethanol + Power, LLC	California	sugarcane	60 (by 2012)	industrial grade CO_2, fertilizer (42)
Ecofin, LCC	Kentucky	corncobs; later corn stover and switchgrass	1.3 (by 2010)	animal feed (31)
Flambeau River Biofuels, LLC	Wisconsin	wood and forest residues	6 (in 2010)	pulp, waxes (12)
Inbicon[3]	Denmark	wheat straw	1.4	"molasses" for animal feed, CO_2 (43)
Iogen Biorefinery Partners, LCC	Saskatchewan	agricultural residues	24 (in 2011)	acetic acid, fertilizer (44)
Lignol Innovations, LTD/ Suncor	Colorado	wood and agricultural residues	2.5 (by 2012)	highly-pure lignin, furfural (31, 21)
SunOpta Bioprocesses, Inc.	Ontario	wood chips	0.5 (2010) 10 (by 2012)	xylitol (22)
Univ. of Florida/ Myriant Tech.	Florida	sugarcane bagasse, rice hulls, wood	400 gal/day (late 2010)	succinic acid, lactic acid (41)
ZeaChem, Inc.	Oregon	wood	0.25 (in 2010)	acetic acid, ethyl acetate, lactic acid, others (15)

[1] Companies stating their production of coproducts (other than lignin for combustion). A more complete list of current cellulosic ethanol projects in the U.S. (as of Sept. 2009) may be found at Reference (12).
[2] other than lignin for combustion.
[3] In November of 2009, Inbicon signed a Memo of Understanding with Great River Energy to develop and construct a 20 million gal/yr biorefinery adjacent to the Spiritwood Station near Jamestown, North Dakota (19).

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Suggested webpages

Review articles on cellulosic ethanol:
http://www.harvestcleanenergy.org/enews/enews_0505/enews_0505_Cellulosic_Ethanol.htm

http://www.nrel.gov/biomass/pdfs/40742.pdf

Animated video of biochemical process (At the end of the animation, hover over each process to read full description.): http://www.inbicon.com/Biomass%20Refinery/How%20it%20works/Pages/How%20it%20works.aspx

Animated video on thermochemical/gasification process: http://www.rangefuels.com/conversion-process.html

All photographs are from the U.S. Department of Energy (DOE) - National Renewable Energy Laboratory (NREL), Photographic Information Exchange, PIX:

http://www.nrel.gov/data/pix/searchpix.html