

Biorefining strategy

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1. Biorefining definition

Biorefining is the sustainable processing of biomass into a spectrum of bio-based products (food, feed, chemicals, and materials) and bioenergy (biofuels, power and/or heat) [Definition IEA Bioenergy Task 42 on Biorefineries].^{1,2}

One can distinguish *product-driven biorefineries* and *energy-driven biorefineries*. In product-driven biorefineries, biomass is fractionalised into bio-based products with maximal added-value and minimal ecological impact, the process residues being used for power and/or heat production, for both internal use and selling of surplus to national grids. In energy-driven biorefineries, biomass is primarily used for the production of biofuels and/or heat, the process residues being sold as feed or being upgraded to added-value bio-based products.

A parallelism can be observed between oil refining and biomass refining. Classic crude oil refinery leads to fuels, building blocks for petrochemistry, and specialty chemicals such as lubricants and solvents. Biomass refinery leads to biofuels, building blocks for agro-bio-chemistry, and specialty chemicals such as biolubricants and biosolvents.

2. Biomass

As a renewable energy source, biomass refers to biological material derived from living, or recently living organisms. Biomass is commonly plant matter. Plants use sunlight to convert water and carbon dioxide into carbohydrates that are stored as chemical energy.

2.1. Chemical composition

The composition of biomass depends upon the plant species:

- Some plants like sugar cane and sugar beet store the chemical energy derived from photosynthesis as simple sugars; they are mostly used for food.
- Other plants store the chemical energy as starch; they include cereal grains such as corn, wheat and rice, and are also mostly used for food.
- Finally, non-food plants such as trees and grasses are composed mostly of *cellulose*, *hemicellulose* and *lignin*. They represent the vast bulk of plant material. The organic matter derived from them is often called lignocellulosic or simply cellulosic biomass. It includes agricultural residues, forestry wastes, a fraction of municipal and industrial wastes, and energy crops such as switchgrass and miscanthus. Such biomass typically contains 40-60% cellulose, 20-40% hemicellulose and 10-25% lignin (figure 1).³

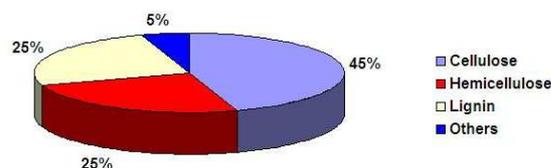


Figure 1 Composition of lignocellulosic biomass

2.2. Plant cell walls

The plant cell wall is an extracellular matrix that encloses each cell in a plant. The cell walls of growing plants are called *primary cell walls*. They are relatively thin and semi-rigid to accommodate subsequent cell growth. Primary cell walls appear to be a network of extended polysaccharides. In higher plants, the dominant feature is the presence of cellulose microfibrils with diameters of ~3 nm, which are crosslinked by single-chain polysaccharides (figure 2).

¹ www.IEA-Bioenergy.Task42-Biorefineries.com

² <http://ie.jrc.ec.europa.eu/events/2009/biorefinery-rrb5.pdf>

³ P. C. BADGER, *An Overview of Ethanol-from-Cellulose*, Appalachian Woody Biomass to Ethanol Conference, Shepherdstown, 2007

Primary cell wall

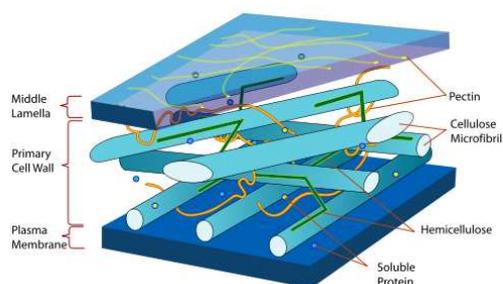


Figure 2 Primary cell wall in plants⁴

Three major classes of polysaccharides have been identified:

- **Cellulose**, which is a linear polymer of glucose units linked together by β 1-4 linkages (figure 3).

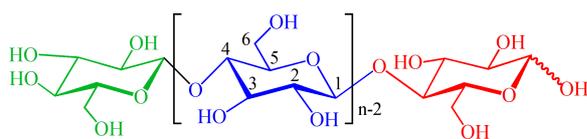


Figure 3 Molecular structure of cellulose

- **Hemicelluloses**, which are branched polymers containing a variety of 5-carbon sugars such as xylose, arabinose and 6-carbon sugars such as glucose, mannose, glucuronic acid, and galactose; they can form hydrogen bonds to the surface of cellulose microfibrils.
- **Pectins**, which are branched or unbranched polymers containing D-galacturonic acid residues; they are found in cell walls especially as gel matrix..

Commonly, once growth stops, a thicker, rigid **secondary cell wall** is constructed by depositing new layers between the primary wall and the plasma membrane. Secondary walls may have a composition similar to that of the primary wall or be notably different. The most common additional polymer in secondary walls is lignin, a complex network of phenolic compounds found in the walls

of the xylem vessels and fibre cells of woody tissues (figure 4).

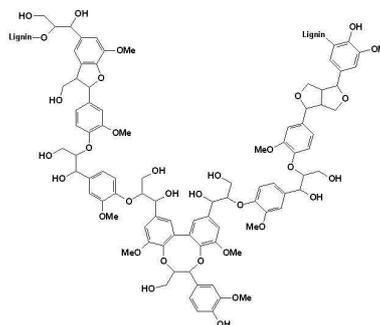


Figure 4 Molecular structure of lignin

When the cell dies, the wall remains.

Even if the cell walls differ in composition and organisation, their underlying structure is remarkably consistent: tough cellulose microfibrils are embedded in a highly crosslinked amorphous matrix.

3. Conversion processes

There are two basic pathways to convert biomass into bioenergy and bio-based products:

- biochemical pathway
- thermochemical pathway

Biochemical conversion primarily involves hydrolysis of the polysaccharides in biomass, and fermentation of the resulting sugars into ethanol. Thermochemical conversion primarily involves gasification or other thermal treatment of the biomass, followed by the catalytic synthesis or the fermentation of the resulting gas or liquid into biofuels. Fuels produced from cellulosic biomass are commonly referred as cellulosic fuels.

3.1 Biochemical conversion

3.1.1 Acid hydrolysis

The **dilute acid** hydrolysis is the oldest technology for converting biomass into ethanol.^{5, 6} Typically a solution of 1% sulphuric acid is used. After more than 100 years of R&D, the process has evolved into the general scheme shown in figure 5.

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http://en.wikipedia.org/wiki/File:Plant_cell_wall_diagram.svg

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http://www1.eere.energy.gov/biomass/printable_versions/dilute_acid.html

⁶ D. I. BRANSBY, *Cellulosic Biofuel Technologies*, Auburn University, 2007

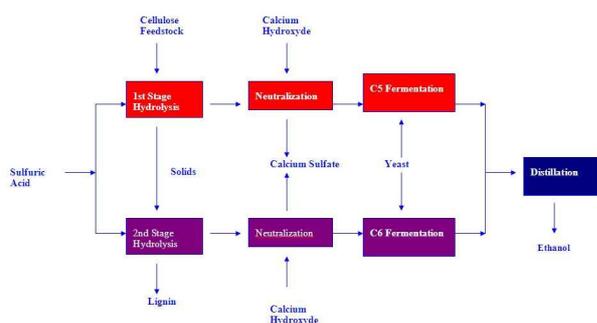


Figure 5 General scheme of two-stage dilute acid hydrolysis

The hydrolysis occurs in two stages to accommodate the differences between cellulose and hemicellulose. Hemicellulose, containing C5 and C6 sugars, is more easily hydrolysable than cellulose, containing only C6 sugars. Furthermore, C5 sugars degrade more rapidly than C6 sugars. With the two-stage process, the first stage can be operated under milder conditions (e.g. 190°), which maximize yield from hemicellulose, whereas the second stage can be optimized (e.g. 215°C) for hydrolyzing the more resistant cellulose. The liquid sugars are recovered at each stage and fermented to ethanol. Lignin and residual cellulose serve as boiler fuel for electricity and steam production.

The **concentrated acid** hydrolysis process has a long history.⁷ The ability to dissolve and hydrolyze native cellulose using concentrated sulphuric acid followed by dilution with water was reported as early as 1883. The concentrated acid disrupts hydrogen bonds, converting cellulose into an amorphous material. Currently, the process is illustrated by the general scheme shown in figure 6.

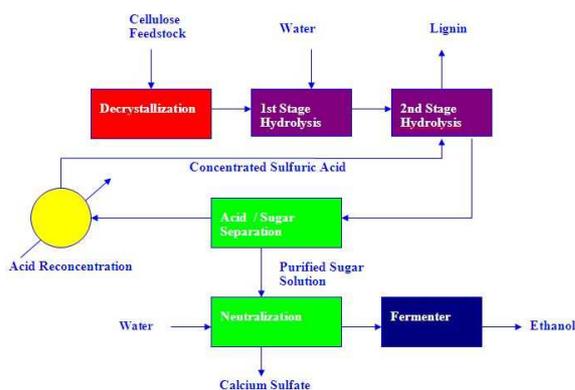


Figure 6 General scheme of the concentrated sulphuric acid process

⁷http://www1.eere.energy.gov/biomass/printable_versions/concentrated_acid.html

The core of the process is the decrystallization followed by the dilute acid hydrolysis.

3.1.2 Enzymatic hydrolysis

An attractive option to breakdown cellulose into sugars is to use cellulose enzymes. A critical factor in the successful commercialization of cellulosic ethanol via enzymatic hydrolysis is the cost of efficient enzymes.⁸

A typical enzymatic process is shown in figure 7.

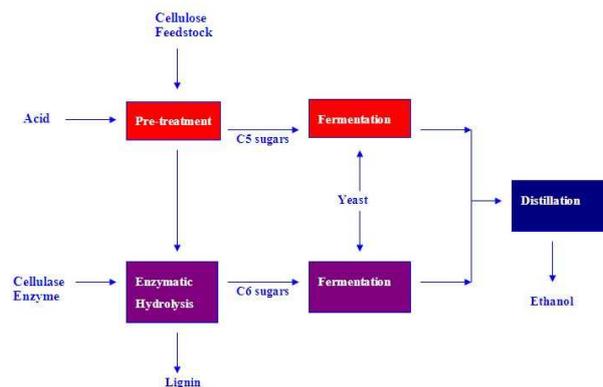


Figure 7 Typical enzymatic hydrolysis process⁸

The process typically includes the following steps: (1) biomass pretreatment typically with steam explosion and dilute acid, where the hemicellulose fraction is broken down into C5 and C6 soluble sugars, (2) enzymatic hydrolysis of cellulose, releasing glucose, (3) glucose fermentation, producing ethanol, (4) pentose fermentation, producing ethanol, and (5) ethanol distillation.⁸

Iogen, a Canadian biotechnology firm, partly owned by Shell, built and operates a demonstration scale facility to convert biomass to cellulosic ethanol using enzyme technology.⁹ This facility is located in Ottawa. Iogen is currently assessing a potential location for a commercial scale cellulosic ethanol plant. Verenum Corporation, a new biofuels industry leader, combines enzyme science with expertise in large-plant infrastructure, evidenced by their pilot and demonstration facilities in Jennings, Louisiana.¹⁰

Challenges for enzymatic technology are: (1) biomass pretreatment, (2) enzyme cost and

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http://www1.eere.energy.gov/biomass/abcs_biofuels.html

⁹

www.iogen.ca/cellulosic_ethanol/what_is_ethanol/process.html

¹⁰ www.verenum.com

efficiency, (3) efficient fermentation of both C5 and C6 sugars, and lignin valorisation.

3.1.3. Product-driven biorefineries

In 2004, a report from the US Department of Energy (DOE) identified *twelve building block chemicals* that can be produced from sugars via biological or chemical conversions.¹¹ The twelve building blocks can be subsequently converted to a number of high-value bio-based chemicals or materials. The twelve sugar-based building blocks are 1,4-diacids (succinic, fumaric and malic), 2-5-furan dicarboxylic acid, 3-hydroxy propionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxybutyrolactone, glycerol, sorbitol and xylitol/arabinitol.

In particular, new bacteria will be used as a biocatalyst to produce succinic acid from biomass (figure 8).¹² The microorganism's metabolic pathways are genetically engineered so they are capable of converting different types of sugar efficiently.

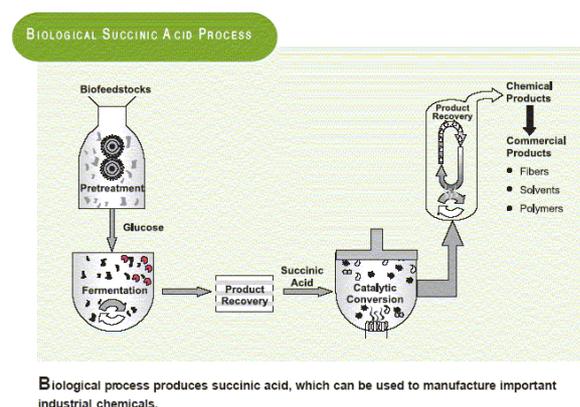


Figure 8 Product-driven biorefinery¹²

3.2 Thermochemical conversion

3.2.1 Primary routes

Primary routes for biomass thermal conversion are schematized in figure 9.¹³

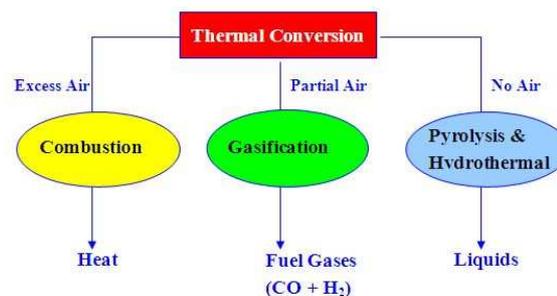


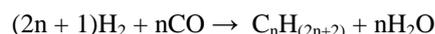
Figure 9 Primary routes for thermochemical conversion

Biomass *combustion* has been one of man's primary ways of deriving energy from biomass. Converting the solid biomass to a gaseous or liquid fuel by heating it with limited oxygen can, however, greatly increase the overall efficiency, and also to make it possible to convert biomass to valuable products. When biomass is heated with less than about one-third the oxygen needed for efficient combustion, it gasifies to a mixture containing essentially carbon monoxide and hydrogen, mixture called synthesis gas or syngas. Biomass can be liquefied by *pyrolysis* and other technologies such as hydrothermal liquefaction. *Gasification* resulting in syngas and pyrolysis resulting in bio-oils are related processes of heating with limited amount of oxygen. Gasification allows a small amount of oxygen, pyrolysis allows virtually none.

3.2.2 Subsequent Fischer-Tropsch process or fermentation

Gasification and pyrolysis are typically followed by the *Fischer-Tropsch* chemical process or fermentation. Combination of biomass gasification and Fischer-Tropsch process is considered as one of the most promising routes to produce biofuels and chemicals.

The Fischer-Tropsch process is a catalyzed chemical reaction in which synthesis gas is converted into liquid hydrocarbons of various forms.¹⁴ The process involves a variety of competing chemical reactions. The most important reactions are those resulting in the formation of alkanes, as described by chemical equations of the form:



In addition to alkane formation, competing reactions result in the formation of alkenes, alcohols and other oxygenated hydrocarbons. Usually, only relatively small amounts of these non-alkane products are formed, although catalysts favouring some of these products have been

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<http://www1.eere.energy.gov/biomass/pdfs/35523.pdf>

¹²

<http://www1.eere.energy.gov/industry/chemicals/pdfs/succinic.pdf>

¹³ R. L. BLAIN, *An introduction to Biomass Thermochemical Conversion*, NREL, 2004

¹⁴ <http://en.wikipedia.org/wiki/Micro-GTL>

developed. In particular, Fischer-Tropsch catalysts can produce a mixture of alcohols which may need to be separated to refine ethanol.

In 2007, Range Fuels announced it will build its first wood cellulosic ethanol plant in Georgia, USA.¹⁵ Range Fuels' process is a two-step thermochemical process including a conversion of biomass to syngas, and a catalytic conversion of the conditioned syngas to alcohols which are then separated and processed to yield a variety of liquid products.

Syngas can also be converted to products in the diesel range using Fischer-Tropsch catalysts. Since 2003, CHOREN Industries (Germany) has been operating a Fischer-Tropsch plant in connection with a biomass gasification unit for the production of diesel.¹⁶ In this plant, the diesel fraction is obtained by distillation of the Fischer-Tropsch raw product. Carbo-V is the patented biomass gasification process of CHOREN. The syngas is then converted into synthetic biofuels using the same Shell Middle Distillate Synthesis (SMDS) that Shell has developed for Gas-to-Liquids production. Shell's SMDS is a low-temperature, cobalt catalyst-based version of the Fischer-Tropsch GTL process.

Microorganisms such as anaerobic bacteria are also used to ferment syngas or bio-oils to fuels such as ethanol. Bioengineering Resources Inc (USA) is involved in the gasification/fermentation technology to produce ethanol.

3.3 Integrated biorefinery

Integrated biorefineries employ various combinations of feedstocks and conversion technologies to produce a variety of products with main focus on producing either biofuels or bio-based products. The combined use of biochemical and thermochemical platforms offers the greatest possibilities for optimizing the conversion of biomass into a variety of fuels, bioenergy in general, and bio-based products (Figure 10).

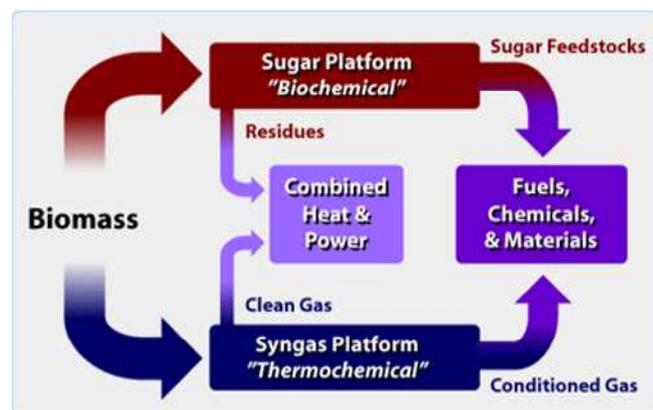


Figure 10 Integrated biorefinery concept.¹⁷

4 Cost and yield estimates

Costs of bioethanol from sugar cane (Brazil), sugar beet (United Kingdom), corn (USA), and cellulose (USA, 2006 and USA, projection 2012) are shown in Table 1.

Table 1 Bioethanol costs

Feedstock	Cost (US \$)
Sugar cane (Brazil)	0.22
Sugar beet (UK)	0.44
Corn (US)	0.30
Cellulose (USA, 2006)	0.59
Cellulose (USA, 2012)	0.28

Table 1 indicates that (1) producing ethanol from sugar beet in the UK costs twice as much as producing it from sugar cane in Brazil, and nearly 45% more than from corn in the USA, (2) the cost of cellulosic ethanol is twice the cost of corn-based ethanol, (3) the cost of cellulosic ethanol should decrease by 50% within 6 years.

Plant yields expressed in tons (t) per hectare (ha) and per year, and ethanol yields expressed in litres (l) per hectare and per year are estimated in Table 2.

Table 2 Plant yield and ethanol yield

Feedstock	Plant yield (t/ha, year)	Ethanol yield per ha per year (l/ha, year)
Wheat/corn	8	2700
Sugar beet	53	3700-5000
Sugar cane	70	4900-6600
Wood (2005)	12	3400-4000
Wood (potential)	25-37	7500-14000
Switchgrass	6-25	4000-10000
Miscanthus	20-61	4000-14000

¹⁵ www.rangefuels.com

¹⁶ www.choren.com

¹⁷ www.nrel.gov/biomass/biorefinery.html

Current bioethanol, produced primarily from simple sugars or starch, is obtained from grains or fruits. In contrast, cellulosic ethanol is obtained from cellulosic materials. Since cellulose is the main component of plants, the whole plant can be harvested, resulting in much better yields per hectare. Even land marginal for agriculture can be planted with cellulose-producing crops such as *switchgrass* (*Panicum virgatum*) and *miscanthus* (*Miscanthus giganteus*), which have the potential to maximize yield per hectare.