

Lignocellulose conversion: an introduction to chemistry, process and economics

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Abstract: Governments across the world are stimulating the valorization of local biomass to secure the energy supply, reduce the emissions of fossil CO₂ and support the rural economy. A first generation of fuels and chemicals is being produced from high-value sugars and oils. Meanwhile, a second generation, based on cheaper and more abundant lignocellulosic feedstock, is being developed. This review addresses the variety of chemistries and technologies that are being explored to valorize lignocellulosic biomass. It shows the need to ‘deoxygenate’ the biomass and reviews the main chemical routes for it, i.e.

- the pyrolysis to char, bio-crude or gas;
- the gasification to syngas and its subsequent conversion, e.g. to alkanes or methanol;
- the hydrolysis to sugar and their subsequent upgrading to oxygenated intermediates via chemical or fermentation routes.

The economics of biomass conversion also needs to be considered: the current production cost of biofuels are typically \$60–120/barrel of oil equivalent. Influential factors include the cost of the biomass at the plant gate, the conversion efficiency, the scale of the process and the value of the product (e.g. fuel, electricity or chemicals).

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Introduction

Governments across the world are stimulating the utilization of renewable energies and resources such as solar, wind, hydroelectricity and biomass. Three major forces are driving them:¹

- Secured access to energy: The world demand for energy is expected to double between years 2000 and 2050. This demand cannot be satisfied by crude oil, natural gas, coal and nuclear energy combined. By its reliance on oil and gas, the world economy is becoming very dependent on a limited number of exporting countries. Renewable

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energies will therefore have to play an increasing role in securing energy throughout the century.

- Threat of climate change: Efforts to reduce the consumption of fossil fuel and capture and sequester the CO₂ will help to reduce CO₂ emissions in the short term. For the long term, however, CO₂-neutral energy sources are needed.
- Develop/maintain agricultural activities: Agricultural economies could be supported by promoting the exploitation of local (bio)resources for food, energy and material.

Interestingly, each of these major drivers also represents one of the three dimensions of sustainability, namely Profitability (affordable energy), Planet (climate change) and People (social stability).

Current use of fossil fuels is split with about three-quarters for heat and power generation, about one-quarter for transportation fuel, and just a few percent for chemicals and materials.² The heat and power sector can be supplied with a variety of renewable sources, namely wind, solar, hydropower and biomass. The transportation sector has a much more limited choice, however. At this time, biomass is the only resource that can provide renewable liquid fuels. Beyond the transportation sector, biomass is also a promising feedstock for the chemical industry.

A first generation of fuels and chemicals is presently produced from sugars, starches and vegetable oils. While instrumental in growing the market, these biofuels are not long-term solutions. First, they compete with food for their feedstock and/or fertile land and are already affecting the price of food. Second, their potential availability is limited by the amount of fertile soil and the yield per hectare. Finally, the effective savings of CO₂ emission and fossil fuel consumption are limited by the energy needed to grow the crop and convert it to biofuel. In the case of corn ethanol, 60–75% of the energy content of ethanol is consumed during its production,^{3–5} 20–25% to grow and harvest the corn and 40–50% to convert it to ethanol.⁵ The latter contribution can be reduced very significantly by using the crop residue as process fuel.

Ways to overcome these three limitations are sought in the utilization of lignocellulosic materials, such as residues from

agriculture and forestry or energy crops. Lignocellulose can be grown in combination with food (e.g. as crop residue) or on non-agricultural lands. The world production (3–5 Gt/year) of these residues could provide 50–85 EJ/year of energy,^{3,6,7} which represents 10–20% of today's world energy demand. The net savings in energy and CO₂ emission are increased by requiring less fertilizer (i.e. less fossil fuels to produce them), fixing CO₂ in the soil (e.g. perennial energy crops) and providing the process fuel as well.

Lignocellulose is much more difficult to convert than sugars, starches and oils. Lignocellulose is the fibrous material that forms the cell walls of the plants 'architecture'. It consists of three major components:^{1,3,8,9}

- Cellulose, which consists of high molecular weight polymers of glucose that are held rigidly together as bundles of fibres to provide material strength. The cellulose typically accounts for some 40 wt% of the lignocellulose.
- Hemicellulose, which consists of shorter polymers of various sugars that glue the cellulose bundles together. It usually accounts for some 25 wt% of the lignocellulose.
- Lignin, which consists of a tri-dimensional polymer of propyl-phenol that is imbedded in and bound to the hemicellulose. It provides rigidity to the structure. It accounts for some 20 wt% of the lignocellulose.

Of course, the lignocellulose also contains a variety of minor components such as proteins, terpenic oils, fatty acids/esters and inorganic materials (mainly based on N, P and K).

Obviously, the structure of lignocellulose is totally different from that of present fuels and chemicals. It needs to be depolymerized and deoxygenated to be suitable for these applications. Deoxygenation is particularly important in the case of fuels as the presence of oxygen reduces the heat content of the molecules and usually gives them high polarity, which hinders blending with present fuels. Full deoxygenation is not always necessary, however, as small amounts of oxygen may provide power or reduce soot formation. Chemical applications may require much less deoxygenation, however, because the presence of oxygen often provides valuable physical and chemicals properties to the product. Deoxygenation can proceed via two main routes, namely the elimination of H₂O and/or the elimination of

CO₂.¹⁰ Interestingly, ideal deoxygenation reactions can proceed with >95% energy efficiency: the reaction products contain >95% of the (lower) heating value of the reactant.¹

Chemistry and processes

A variety of chemistries and processes can be applied to convert lignocellulosic materials to valuable fuels and chemicals.^{3,11} For instance, thermal reactions are exploited in the pyrolysis of biomass to charcoal, oil and/or gases and its gasification to synthesis gas and/or hydrogen. All these products can be used without further processing to provide heat or power. Moreover, the synthesis gas and, in some cases, the pyrolysis oil can also be converted to high-quality liquid fuels. Alternatively, lignocellulose can also be hydrolysed to liberate the lignin and depolymerize the polysaccharides to sugars. The sugars can subsequently be converted to a variety of fuel and chemical components via chemical or biological routes. All these conversions involve complex reactions of the carbohydrate, the lignin and, eventually, between carbohydrates and lignin. In this short review, these processes will be discussed, limited to the reactions of the main constituent, i.e. the carbohydrates. The chemistry of lignin conversion will not be considered here. Obviously, lignocellulose and lignin-rich process residues can be burned directly to provide heat, power or steam; however, the related chemistry and technologies is not part of this review.

Pyrolysis

Chemistry

Pyrolysis has a long history in the upgrading of biomass. The dry distillation of hardwood was applied in the early 1990s to produce organic intermediates (methanol and acetic acid), charcoal and fuel gas.³ Today's processes can be tuned to form char, oil and/or gas, depending on the temperature and reaction time, from ~300°C and hours, to 400–500°C and minutes or seconds, on to >700°C and fractions of a second.^{3, 11–13} The process is typically carried out under an inert atmosphere. The basic chemistry of pyrolysis will be illustrated by focusing on the conversion of carbohydrate components (Fig. 1).

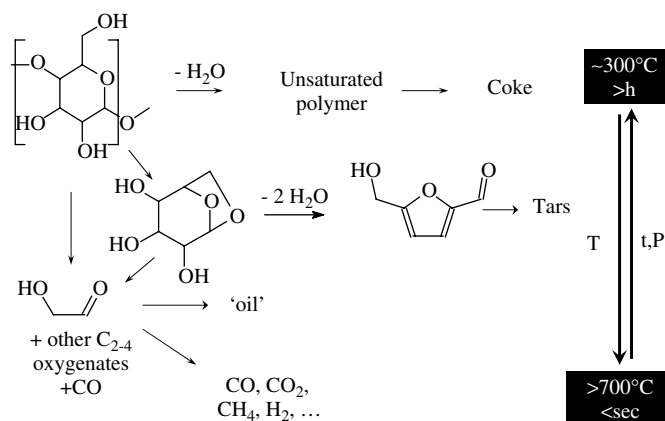


Figure 1. Pyrolysis of biomass.

When heated at low temperatures (<200°C) for extended reaction times (hours), the carbohydrate polymers partially depolymerize to short chains of some 200 sugar units.^{13,14} Upon heating at higher temperatures (~300°C), however, the depolymerization is accompanied by slow dehydration to unsaturated species, which can undergo subsequent reactions to form unsaturated polymers and, eventually, char.¹⁴ When heated at higher temperatures, the depolymerization reactions can be pushed to the point of liberating volatile species, which can again lead to the formation of tars if they are efficiently removed from the medium. At even higher temperatures, extensive C–C bond breaking occurs, which leads to the formation of various C_{2–4} oxygenates and, beyond 700°C, to a mixed gas of moderate heating value, namely to a mixture of CO, CO₂, H₂ and CH₄.

Product applications

The char produced by pyrolysis is typically light and porous. It has a high energy content (~30 GJ/t), which makes it a valuable fuel for industrial and consumer applications. The gases have a moderate energy content, and can be used for generating heat or electricity.

The pyrolysis oil is a very complex and multiphase mixture of low and high molecular weight components, including water (~25%), a variety of organic oxygenates and polymeric carbohydrate and lignin fragments.¹⁵ Pyrolysis oil is, therefore, unstable, highly acidic, partly water-soluble and has a low energy content (~17 GJ/t). It is therefore a low-quality fuel. It can be used for generating heat or power.

To be used as transportation fuel, however, the pyrolysis oil needs further upgrading, e.g. by means of hydro- or catalytic cracking.⁷ 'BioCoup', a European consortium of 17 research laboratories, including Shell's, has been put in place to develop technologies for co-processing biobased liquids, such as pyrolysis oil, in standard refinery units.

Processes and alternative developments

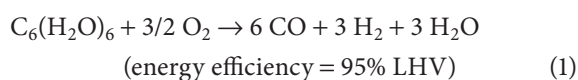
A variety of pyrolysis processes has been reported in the literature. The designs usually aim at satisfying three criteria: (1) a high temperature to enable cracking and decomposition reactions; (2) a large heat supply to drive them; and (3) a short residence time to minimize the condensation of volatile products.

The pyrolysis can also be carried out in a variety of liquid and/or gas media that function as heat carrier, dispersing medium and/or reactive medium. For instance, pyrolysis can be performed in an aqueous medium at high temperature and pressure, as applied in the HydroThermal Upgrading (HTU) process, which was developed in the Shell laboratories in the 1980s.¹⁶ The aqueous-phase pyrolysis can also be assisted by catalysts (e.g. Na₂CO₃) and reactive gases (e.g. synthesis gas), as in the case of the Pittsburgh Energy Research Center (PERC) process.^{3,17} Supercritical solvents can be applied as reactive dispersing medium at milder temperatures and high pressures, i.e. 200–350°C and >100 bar.^{7,18–20}

Gasification

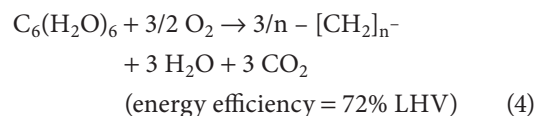
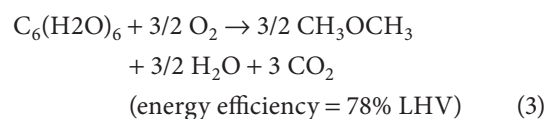
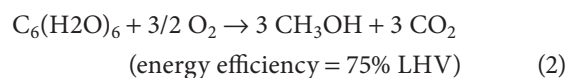
Chemistry

As discussed above, the pyrolysis of biomass results in the formation of synthesis gas, a valuable mixture of CO and H₂. The formation of synthesis gas is endothermic and proceeds best at high temperature (>1000°C). This is conveniently achieved by co-feeding some oxygen to burn about 25% of the feed in the reaction:



(LHV: low heating value released by burning a fuel to CO₂ and H₂O vapour, without steam condensation.) The

resulting synthesis gas can subsequently be converted to methanol or dimethyl ether or be 'polymerized' to a mixture of hydrocarbons via Fischer–Tropsch synthesis according to the overall reactions equations:^{21, 22}



These simple and fairly ideal equations reveal that the conversion of sugars to alkanes or methanol proceeds at best with carbon and energy efficiencies of 50% C or ~75% LHV. Any yield loss in the gasification of the conversion step results in a further drop in efficiency. Of course, synthesis gas can also be used as a source of hydrogen for use as fuel or for deoxygenating biobased products (e.g. pyrolysis oil).

Process

Numerous gasification processes have been proposed. They vary in the use of air (for power generation) or pure oxygen (for methanol or Fischer–Tropsch synthesis), the reactor design and the removal of contaminants (e.g. tars, ash and inorganic volatile components, such as NH₃ and HCl) from the synthesis gas.^{3,12} Similarly, several conversion loops have been proposed to convert the synthesis gas to methanol or alkanes. Important design elements include the adjustment of the H₂/CO ratio of the synthesis gas and the reactor design.^{21,22}

A process design, based on CHOREN's gasification technology²³ and Shell's Fischer–Tropsch technology,²⁴ is currently being demonstrated at 15 kt/a scale in Germany. It consists of a pyrolysis reactor followed by an O₂-fed gasifier. The resulting synthesis gas is then cooled, cleaned, 'shifted' to the desired H₂/CO ratio and introduced into the Fischer–Tropsch reactor for conversion to high-quality alkanes.

Hydrolysis and sugar conversion

Chemistry of hydrolysis

Biomass does not necessarily require the severe conditions applied during pyrolysis or gasification to be converted. Polysaccharides and lignin are bound through reactive ether links, i.e. ketal and aryl-ether links, that are prone to hydrolysis. Indeed, the lignin and hemicellulose readily hydrolyses at mild temperatures (<150°C) in the presence of acids or bases. The crystalline structure of the cellulose hinders catalyst access to the ether links. More severe conditions are therefore required for full depolymerization.

In the presence of excess water, the polysaccharides can be hydrolysed to liberate the individual sugars together with their isomers and oligomers (Fig. 2). This hydrolysis reaction is catalysed by acids and bases. At a given temperature, consecutive decomposition reactions take place, leading to furan species, such as furfural and hydroxymethyl furfural, which easily condense to tars, or to levulinic acid and formic acid.^{8, 25–28} All these reactions contribute to lowering the yield in sugars during hydrolysis. Moreover, several degradation products, such as furfural and hydroxymethyl furfural, are inhibitors for downstream fermentation.

Chemical conversion of sugars

The hydrolysis reaction can be geared to produce sugar mixtures, which are subsequently converted to a variety of derivatives through chemical or biological conversion. The fermentation of sugars is discussed in the following subsection. Chemical technologies also offer a large variety of possibilities to upgrade the sugars. Sugars can be hydrogenated to C_{5–6} polyols (or sugar alcohols) such as xylitol, mannitol and sorbitol,^{8,25} hydrogenolysed to C_{2–3} glycols,^{29,30} or further upgraded via oxidation or halogenation reactions.³¹ Sugars can be used for detergent manufacture or converted to N-heterocyclic components, pyrones and aromatics.²⁵

Alternatively, the hydrolysis can be geared towards the direct production of derivatives, such as furfural, hydroxymethyl furfural and/or levulinic acid. These derivatives can be further converted to a variety of chemical intermediates.^{8,25–28,32}

Fermentation of sugars

Lifeforms have developed efficient metabolisms to oxidize sugars back to H₂O and CO₂ to provide the energy required for organism growth. In the absence of oxygen, however, organisms have developed alternative metabolisms that stop

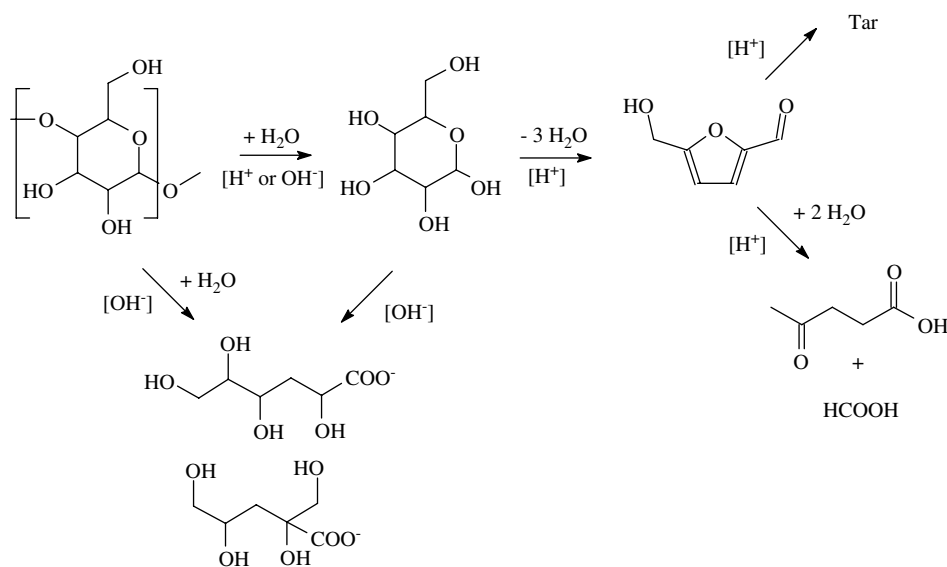


Figure 2. Biomass hydrolysis in acidic and basic medium.

at less oxidized stages and, thereby, deliver less energy. This is the case for baker's yeast, which stops its metabolism at ethanol.

The conversion of glucose (Fig. 3) proceeds via pyruvic acid and acetaldehyde (bound to the coenzyme-A) to ethanol. The overall reaction delivers therefore two molecules of ethanol and two molecules of CO₂ for every glucose unit. The metabolic pathways can be diverted to other products, however (Fig. 3). For instance, the pyruvic acid intermediate can be rehydrogenated to lactic acid, which is the building block for Cargill's polylactate polymer.³³ Alternatively, the acetaldehyde intermediates can be oxidized to acetic acid and CO₂/CH₄ by methanogenic organisms, which is the biogas that emanates from dormant waters or waste landfills.³

Process and recent developments

The older hydrolysis processes applied concentrated inorganic acids such as H₂SO₄ and mild temperature (100–120°C) to minimize the undesired consecutive reactions.³⁴ The recovery and reconcentration of the acid catalyst turned out to be difficult and expensive. Modern processes are therefore based on diluted acid operating at higher temperatures (180–220°C) or on cocktails of enzymes operating at mild temperature.³⁴ The cellulose enzymes are much bulkier than homogeneous acids or bases, however. They therefore encounter difficulties in properly reaching and

hydrolysing the hemicellulose and the lignin. Mechanical and chemical pre-treatments are usually required to open up the structure of the lignocellulose to enable the enzymes to hydrolyse its constituents.³⁴

Other processes target selective hydrolysis of the lignocellulose to extract the lignin and hemicellulose constituents and produce a clean cellulosic residue, e.g. for the paper industry. The Kraft pulping process is the most broadly applied one.⁹ However, a variety of organic solvents is being investigated as well; for instance mixtures of formic and/or acetic acid with aqueous HCl³⁵ or solutions of ethanol/water with diluted H₂SO₄.³⁶ The resulting pulp and/or sugar solution can then be applied for fermentation to ethanol after neutralization and purification.

An example of combined hydrolysis and fermentation is the process developed by Iogen to convert lignocellulosic materials, such as wheat straw, to ethanol.³⁷ The straw is chopped and milled prior to a 'steam-explosion' pre-treatment to open up the cellulosic structure. The resulting pulp is subsequently impregnated by a specific enzymatic solution to hydrolyse the lignocellulose. Lignin is precipitated and used to generate electricity to supply the plant. The lignin-free liquor is then fermented to ethanol using a microorganism that ferments the glucose as well as the C₅ xylose. Shell has taken a minority share in Iogen Biorefinery to demonstrate the technology through a 54 kt/a plant to be constructed at Shelley, Idaho.

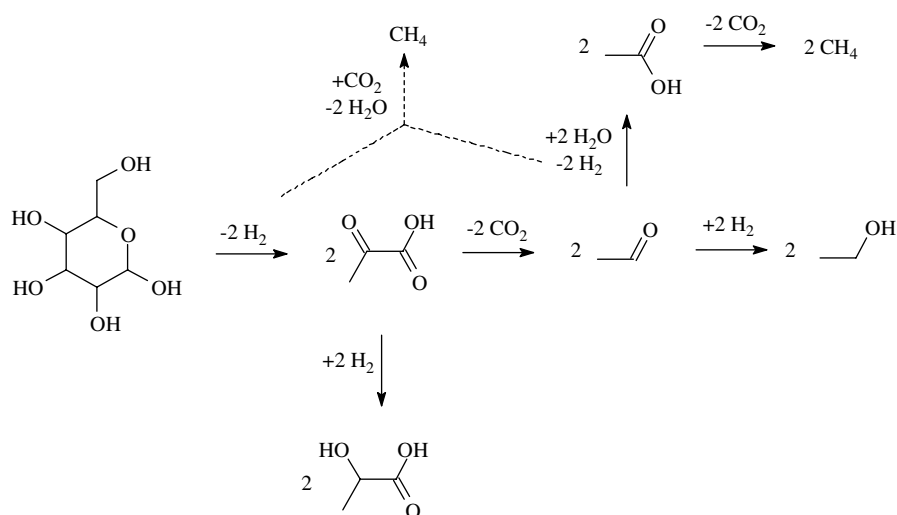


Figure 3. Biomass fermentation.

Shell is also exploring new fermentation routes to biofuels via a partnership with Codexis, an American gene reshuffling company, and active participation in the Dutch biotechnology consortium B-BASIC.

Economics

Numerous studies have discussed the economics of biomass conversion processes over the last 20–30 years. Some of these studies have been revisited and compiled using a single base and a single set of assumptions.¹ For this purpose, the manufacturing costs have been split into two major contributions, namely the feed and the processing costs. The former covers the cost of purchasing the feedstock. The latter covers the cost of installing and running the manufacturing plants, i.e. the cost of the plant, the labour as well as the energy and chemicals consumed. The economics of the various technologies can then be visualized by plotting the processing cost against the feed of the various process alternatives, as done in Fig. 4. The diagonal 'eco-cost' lines represent overall manufacturing cost.

Figure 4 displays processes that produce transportation fuels from bio and fossil feedstock, i.e. from lignocellulose, starch and vegetable oil as well as from crude oil and natural gas. It shows that the cost of oil refining is dominated by feed cost whereas the costs of gas conversion (e.g. MeOH or Fischer–Tropsch synthesis) are dominated by technology. Similarly, biofuels derived from vegetable oils are dictated by feed cost whereas those derived from lignocellulose

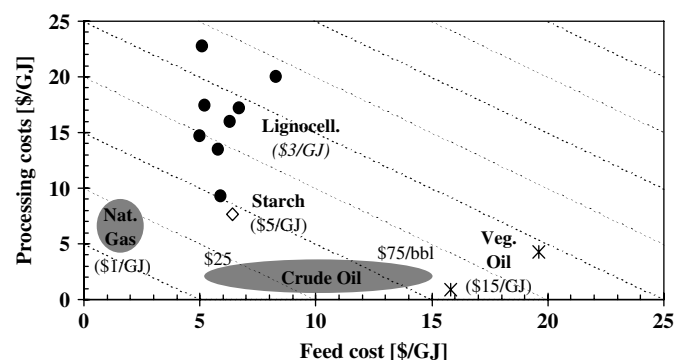


Figure 4. Feed and processing cost of transportation fuels derived from lignocellulose and fossil resources (the biofuel plants are set at 400 MW intake, which corresponds to ~680 kt/a of lignocellulose¹).

are dominated by technology. The economics of biofuels derived from starch and sugars is intermediate to these two extremes. There is obviously a trade-off between feedstock cost and plant cost. Feedstocks, such as vegetable oil, may be expensive (\$13–18/GJ or \$500–700/t) but they are easy to convert. Others like lignocellulose may be cheap (\$2–4/GJ or \$34–70/t dry) but are very difficult to convert.

The diagonal lines also indicate that production of biofuels typically cost \$15–25/GJ, which exceeds the \$5–15/GJ of fossil fuels. Biofuels appear to be competitive with oil refining only at high oil prices, say \$50–75/bbl.

Despite the high processing costs, the cost of the biomass conversion plants reported in the literature appeared to follow the same general laws as those of chemical and fuel plants:^{38,39} irrespective of the technology applied, the plant cost of biofuel plants correlates with the overall energy loss of the plant exactly as do other chemical and fuel plants.¹ It is then not surprising to see the cost of biomass conversion plants decreasing with increasing energy efficiency, after recalculation to a single plant size of 400 MW intake (i.e. ~680 kt/a lignocellulose) (Fig. 5).

Based on the analysis presented above, it is imperative to reduce the processing cost of lignocellulosic feedstock. Improvements could be sought in the overall energy demand of the plant. One could, for instance, look at the handling and pre-treatment of solid feedstock, which require heavy and energy-consuming equipments. The purification of the product can also be energy- and capital-intensive. For instance, hydrolysis and fermentation

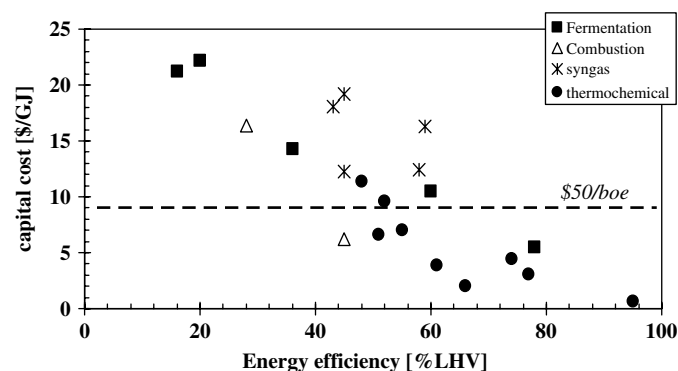


Figure 5. Capital cost of biomass conversion plants (400 MW intake, 25% capital charge, \$2005¹).

technologies often result in a product that is highly diluted in water and requires expensive recovery by distillation or extraction.

Equally important is to increase the scale of the process as much as possible. The contribution of the plant cost to the overall manufacturing cost is known to decrease by 20–25% for a two-fold increase in plant size. However, the scale of biofuel plants might not be limited by technology but rather by the amount of feedstock that can be collected within a reasonable radius and transported to the plant at reasonable cost. In fact the intake of 400 MW (or ~680 kt/a of lignocellulose) assumed here requires a fairly large collection area of some 6000 km², as discussed by Hettenhaus.⁴⁰

The analysis here was limited to the manufacture of finished biofuels. The economics of converting the biomass to biocrude, electricity or chemicals was omitted for the sake of simplicity but is discussed elsewhere.¹ Accordingly, biocrude may compete with fuel oil at an oil price of \$50–80/bbl, biofuel may compete with gasoline and diesel at \$70–110/bbl, and green-electricity is affordable at \$80–100/bbl oil.

In contrast to fuels and power, the conversion to chemicals cannot be expressed with a general break-even oil price. It is, however, important to notice that chemical intermediates are promising products for biomass conversion for the following reasons:

- Many chemical intermediates already contain some oxygen and, thus, would require only partial deoxygenation of the biomass.
- They often require complex and wasteful manufacturing processes, when starting from crude oil.⁴¹ Biomass may offer simpler and/or cleaner manufacturing routes.
- They are typically >10 times as valuable as fuels, on a carbon base, which leaves more economic room to manufacture them from biomass.
- They are produced at a scale that is close to that of biomass conversion plants.

Obviously, manufacturing plants could combine the production of fuels and chemicals, including high-value specialties that are extractable from the feedstock, to improve profitability.

These various reasons explain why numerous research groups are exploring the conversion of biomass to chemical intermediates.

Summary and conclusions

Lignocellulose biomass is a mixture of phenolic lignin and carbohydrates – cellulose and hemicellulose. It is growing abundantly on earth and is largely available as agricultural and forestry residues.

Lignocellulose can be converted via three major routes:

- pyrolysis to a complex and unstable oil with some gas and char;
- gasification and subsequent conversion to electricity or to liquid products, such as alkanes or methanol;
- hydrolysis to sugars with subsequent transformation to fuels and chemicals via chemical conversion or fermentation.

Obviously, these routes can also be combined. For instance, lignin-rich residues from hydrolysis can be converted to fuels by means of pyrolysis or gasification.

Lignocellulose conversion processes are still expensive today, being competitive at crude oil prices between \$50 and \$100/bbl. Lignocellulose might be a fairly cheap feedstock, cheaper than crude oil. However its conversion requires large investments. Cost reduction is imperative for lignocellulose to play a role as feedstock for fuel and chemicals. It will require simpler and less energy-demanding processes, improved infrastructure for collecting the biomass over a large area and improved agricultural and forestry practices that provide residual biomass in significant amounts without deteriorating the soil over the long term. Cost reduction will not rely only on technological breakthrough. It will also be achieved by continuous incremental improvements as the technologies are deployed and mature.

The conversion of lignocellulose to energy, fuels and chemicals is attracting much interest throughout the world. There is much political support for utilizing it for biofuels. This is clearly illustrated by the \$385 million that the US Department of Energy has recently reserved for co-funding six cellulosic ethanol plants. Utilization of lignocellulose

for energy and chemicals would be more sensible, however. Compared to biofuels, direct combustion of lignocellulose makes more efficient use of its energy content, whereas its conversion to chemicals could make more efficient use of its mass or atoms.

Shell is present and active in numerous biofuel areas. It is stimulating the biofuel market by being the world's biggest trader in first-generation biofuels, i.e. bioethanol and biodiesel. For instance, it sold more than 3 billion litres of biofuels in 2005. Shell is also exploring and developing technologies for manufacturing second-generation (cellulosic) biofuels through partnership and independent research. Shell's partnerships are aiming at

- upgrading pyrolysis oil to transportation fuel within the 'BioCoup' consortium;
- producing diesel via gasification and Fischer-Tropsch synthesis with CHOREN;
- producing cellulosic ethanol with Iogen;
- exploring new biotechnologies for biofuels with Codexis and within the 'B-BASIC' consortium.

References

1. Lange JP, Lignocellulose conversion: an introduction to chemistry, process and economics, in *Catalysis for Renewables*, ed by Centi G and van Santen R. Wiley-VCH, Weinheim (2007).
2. US Department of energy, Energy Information Administration, *International Energy Outlook 2006*, <http://www.eia.doe.gov>
3. Klass DL, *Biomass for Renewable Energy, Fuels and Chemicals*, Academic Press, London (1998).
4. Farrell AE, Plevin RJ, Turner BT, Jones AD, O'Hare M, Kammen DM, Ethanol can contribute to energy and environmental goals. *Science* **311**: 506 (2006).
5. Hammerschlag R, Ethanol's energy return on investment: a survey of the literature 1990–present. *Env Sci Technol* **40**: 17446 (2006).
6. Okkerse C, van Bekkum H, From fossil to green. *Green Chem*, **1**: 107–114 (1999).
7. Dale BE and Kim S, Biomass refining global impact – the biobased economy of the 21st century, in *Biorefineries – Industrial Processes and Product*, Vol. 1, ed by Kamm B, Gruber PR, Kamm M. Wiley-VCH, Weinheim, pp. 41–66 (2006).
8. Kamm B, Kamm M, Schmidt M, Hirth T, Schulze M, Lignocellulose-based chemical products and product family trees, in *Biorefineries – Industrial Processes and Product*, Vol. 2, ed by Kamm B, Gruber PR, Kamm M. Wiley-VCH, Weinheim, pp. 97–149 (2006).
9. Sjöström E, *Wood Chemistry, Fundamental and Applications*, 2nd edn. Academic Press, London (1993).
10. Petrus L, Noordermeer MA, Biomass to biofuels - a chemical perspective. *Green Chem* **8**: 861–874 (2006).
11. Huber GW, Iborra S, Corma A, Synthesis of transportation fuels from biomass – chemistry, catalysts and engineering. *Chem Rev* **106**: 4044–4099 (2006).
12. Brown RC, Biomass refineries based on hybrid thermochemical-biological processing – an overview, in *Biorefineries – Industrial Processes and Product*, Vol. 1, ed by Kamm B, Gruber PR, Kamm M. Wiley-VCH, Weinheim, pp. 227–252 (2006).
13. Antal MJ, Biomass pyrolysis – a review of the literature, part I, carbohydrate pyrolysis. *Adv Solar Energy* **1**: 61–111 (1983).
14. Lomax JA, Commandeur JM, Arisz PW, Boon JJ, Characterisation of oligomers and sugar ring-cleavage products in the pyrolysate of cellulose. *J Anal Appl Pyrolysis* **19**: 65–79 (1991).
15. Mohan D, Pittman CU, Steele PH, Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy Fuels* **20**: 848–889 (2006).
16. Goudriaan F, van de Beld B, Boerefijn FR, Bos GM, Naber JE, van der Wal S, Zeevalkink JA, Thermal efficiency of the HTU process for biomass liquefaction, in *5th Conference on Progress in Thermochemical Biomass Conversion*, Tyrol, Austria, September 2000, Vol. 2, ed by Bridgwater AV, pp. 1312–1325 (2001).
17. Thigpen PL, Berry WL, Liquid fuels from wood by continuous operation of the Albany, Oregon biomass liquefaction facility, in *Energy from Biomass and Wastes VI*, ed by Klass DL. Institute of Gas Technology, Chicago, pp. 1057–1095 (1982).
18. Köll P, Brönstrup B, Metzger JO, Liquefaction of biomass with supercritical fluids in high pressure/high temperature flow reactor, in *Chemical engineering at supercritical fluid conditions*, ed by Paulaitis ME, Penninger JML, Gray RD Jr, Davidson P, Ann Arbor Science, Ann Arbor, MI (1983).
19. Poirier MG, Ahmed A, Grandmaison JL, Kaliaguine SCF, Supercritical gas extraction of wood with methanol in a tubular reactor. *Ind Eng Chem Res* **26**: 1738–1743 (1987).
20. Minami E, Saka S, Comparison of the decomposition behaviors of hardwood and softwood in supercritical methanol. *J Wood Sci* **49**: 73–78 (2003).
21. Lange JP, Methanol synthesis: a short review of technology improvements. *Catal Today* **64**: 3–8 (2001).
22. Moulin JA, Makkee M, van Diepen A, *Chemical Process Technology*, Wiley, New York (2001).
23. CHOREN, <http://www.choren.com>
24. Sie ST, Senden MMG, van Wechem HMH, Conversion of natural gas to transportation fuels via the Shell Middle Distillate Synthesis process (SMDS). *Catal Today* **8**: 371–394 (1991).
25. Lichtenthaler FW, The key sugars of biomass: availability, present non-food uses and potential future development lines, in *Biorefineries – Industrial Processes and Product*, Vol. 2, ed by Kamm B, Gruber PR, Kamm M. Wiley-VCH, Weinheim, pp. 3–59 (2006).
26. Hayes DJ, Fitzpatrick S, Hayes MHB, Ross JRH, The biofine process – production of levulinic acid, furfural and formic acid from lignocellulosic feedstock, in *Biorefineries – Industrial Processes and Product*, Vol. 1, ed by Kamm B, Gruber PR, Kamm M. Wiley-VCH, Weinheim, pp. 139–164 (2006).

27. Bozell JJ, Moens L, Elliott DC, Wang Y, Neuenschwander GG, Fitzpatrick SW, Bilski RJ, Barnefeld JL, Production of Levulinic acid and use as a platform chemical for derived products. *Resources, Conservation Recycling* **28**: 227–239 (2000).
28. Timokhin BV, Baransky VA, Eliseeva GD, Levulinic acid in organic synthesis. *Russ Chem Rev* **68**: 73–84 (1999).
29. Crabtree SP, Lawrence RC, Tuck MW, Tyers DV, Optimize glycol production from biomass. *Hydrocarbon Process (2)*, **2**: 87–92 (2006).
30. Elliott DC, Process optimization for polyols production from glucose, Final Report CRADA with International Polyol Chemicals Inc. and Pacific Northwest National Laboratory, PNNL-11476, Pacific Northwest National Laboratory, Richland, Washington (1997).
31. de Wit D, Maat L, Kieboom APG, Carbohydrates as industrial raw materials. *Ind Crops Products* **2**: 1–12 (1993).
32. Moreau C, Belgacem MN, Gandini A, Recent catalytic advances in the chemistry of substituted furans from carbohydrates and in the ensuing polymers. *Topics Catal* **27**: 11–30 (2004).
33. Gruber P, Henton DE, Starr J, Polylactic acid from renewable resources, in *Biorefineries – Industrial Processes and Product*, Vol. 2, ed by Kamm B, Gruber PR, Kamm M. Wiley-VCH, Weinheim, pp. 381–407 (2006).
34. Katzen R, Schell DJ, Lignocellulosic feedstock biorefinery: history and plant development for biomass hydrolysis, in *Biorefineries – Industrial Processes and Product*, Vol. 1, ed by Kamm B, Gruber PR, Kamm M. Wiley-VCH, Weinheim, pp. 129–138 (2006).
35. Lehnen R, Saake B, Nimz HH, Furfural and hydroxymethylfurfural as by-products of FORMACELL pulping. *Holzforschung* **55**: 199–204 (2001).
36. Pye EK, Industrial lignin production and applications, in *Biorefineries – Industrial Processes and Product*, Vol. 2, ed by Kamm B, Gruber PR, Kamm M. Wiley-VCH, Weinheim, pp. 165–200 (2006).
37. Tolan JS, Iogen's demonstration process for producing ethanol from cellulosic biomass, in *Biorefineries – Industrial Processes and Product*, Vol. 1, ed by Kamm B, Gruber PR, Kamm M. Wiley-VCH, Weinheim, pp. 193–208 (2006); see also <http://www.iogen.ca>
38. Lange JP, Tijm PJA, Process for converting methane to liquid fuels: economic screening through energy management. *Chem Eng Sci* **51**: 2379–2387 (1996).
39. Lange JP, Fuels and chemicals manufacturing – guidelines for understanding and minimizing the production costs. *CatTech* **5**: 82–95 (2001).
40. Hettenhaus J, Biomass commercialization and agriculture residue collection, in *Biorefineries – Industrial Processes and Product*, Vol. 1, ed by Kamm B, Gruber PR, Kamm M. Wiley-VCH, Weinheim, pp. 317–344 (2006).
41. Lange JP, Sustainable development: efficiency and recycling in chemicals manufacturing. *Green Chem* **4**: 546–550 (2002).