

ENGINEERING JOURNAL

Editorial

Bioethanol Production from Cellulose and Biomass-Derived Syngas

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ENGINEERING JOURNAL Volume 16 Issue 5

Received 23 September 2012

Accepted 25 September 2012

Published 1 October 2012

Online at <http://www.engj.org/>

DOI:10.4186/ej.2012.16.5.1

Global consumption of energy, particularly fossil fuels, has increased exponentially in recent times. As a result, the release of trapped carbon from these fuels has led to growing concern about global warming. Regardless of the controversy of anthropogenic global warming, present petroleum consumption rate is unsustainable. New and innovative ways at harnessing energy have been and are being developed. Renewable energy sources such as solar and wind energy have slowly but surely supplemented energy generated from fossil fuels. However, it is difficult to integrate these renewable energy sources with the current generation of automobiles. One recent development is to mix ethanol produced from plant material or biomass into gasoline. Vehicles have also been designed to run on pure ethanol as well. Ethanol produced from various renewable sources of biomass should be used in a sustainable way.

Ethanol is a volatile and colourless liquid with a low viscosity of 0.0012 Pa.s and density of 0.789 g/cm³ at 20°C [1]. Its vapor has a slight odour and burns with a colourless flame that is hardly visible in normal light. The combustion products of ethanol are harmless water and carbon dioxide. This makes ethanol a very attractive fuel in place of gasoline. Since ancient times, ethanol has been produced in the form of alcoholic beverages by the fermentation of sugar. However, the obtained concentration was too low to be used in gasoline engines. Distillation was first recorded in the School of Salerno in Italy in the 12th century and pure alcohol was first mentioned in Spain [2]. Because of the existence of azeotropic point, ethanol cannot be further concentrated by conventional distillation and it was not until the end of the 18th century when pure ethanol could be obtained [3].

Production of ethanol from biological feedstock was first achieved in Germany using wood in 1898. In the Scholler process, dilute sulfuric acid was pumped through a bed of wood chips, thereby hydrolyzing cellulose to glucose, which is then fermented to produce ethanol [4]. Nowadays, bioethanol could be produced from non-crop biomass by two distinct processes: cellulolysis & fermentation (a biological approach) and gasification (thermochemical approach) [5]. In the former, cellulose material is first hydrolyzed to simple sugars which are then fermented to yield ethanol which is further concentrated by distillation. In gasification, cellulose material is first converted into carbon monoxide and hydrogen (syngas), which are then converted to ethanol by either chemical catalysis or fermentation.

Next, we look into these two approaches in more details. The first step in the biological approach is the pretreatment of the biomass raw material. The bulk of plant material is lignocelluloses. The cellulose is protected from hydrolysis by lignin. Therefore the structure has to be broken to free the cellulose. This can be done by various physical and chemical methods. The Organosolv and Sulfite Pretreatment to Overcome Recalcitrance of Lignocelluloses (SPORL) is highly effective in terms of cellulose conversion for feedstocks with high lignin content [6]. A mechanical alternative is steam explosion which involves subjecting the biomass to high-pressure steam for a certain period of time and then explosively release the pressure.

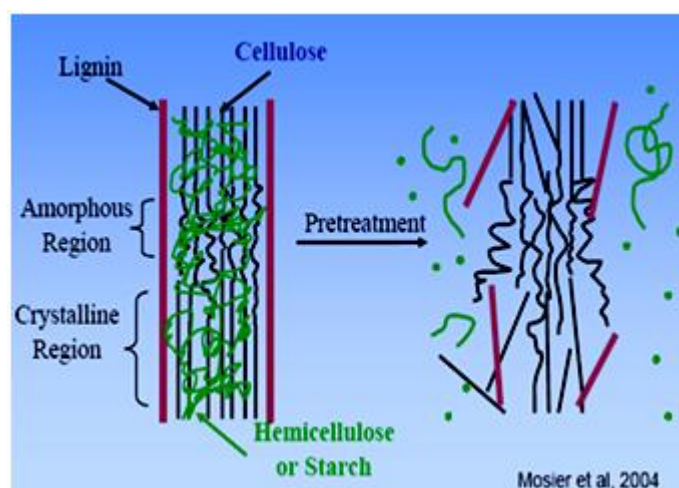


Fig. 1. Cellulose released from lignin structure during pretreatment.

In cellulolysis, the 1,4-beta-D-glycosidic linkages in cellulose are broken by either chemical or enzymatic hydrolysis. Here only enzymatic hydrolysis will be introduced [7]. Cellulose molecules can be broken into glucose by various cellulase enzymes found naturally in grazing animals such as cows and sheep. These enzymes can also be harvested from genetically engineered fungus, along with xylanase and

hemicellulase enzymes, which can be used on plant feedstock to produce sugars for fermentation [8]. The hydrolysis is typically carried out at around 50°C and pH 5.

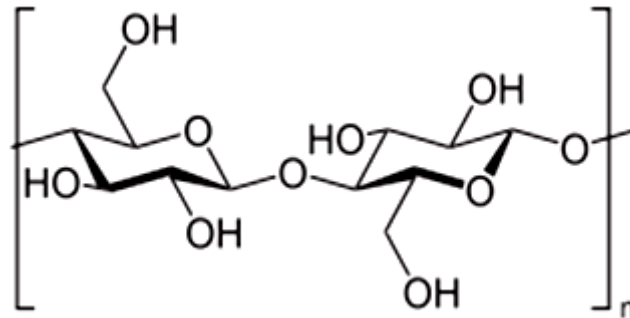


Fig. 2. Cellulose with glycosidic linkages.

There are generally 5 types of cellulases and they are categorised according to the reactions they catalyze.

- Endocellulase – cleaves internal bonds and creates new cellulose chain ends.
- Exocellulase – cleaves 2 or 4 units from either end of a cellulose chain, thereby creating disaccharides or tetrasaccharides, respectively.
- Cellobiase – hydrolyzes tetrasaccharides or disaccharides into monomers such as glucose.
- Oxidative cellulases – depolymerizes cellulose by radical reaction.
- Cellulose phosphorylases – depolymerizes cellulose using phosphates instead of water.

The main reactions carried out by the enzymes listed above are illustrated below.

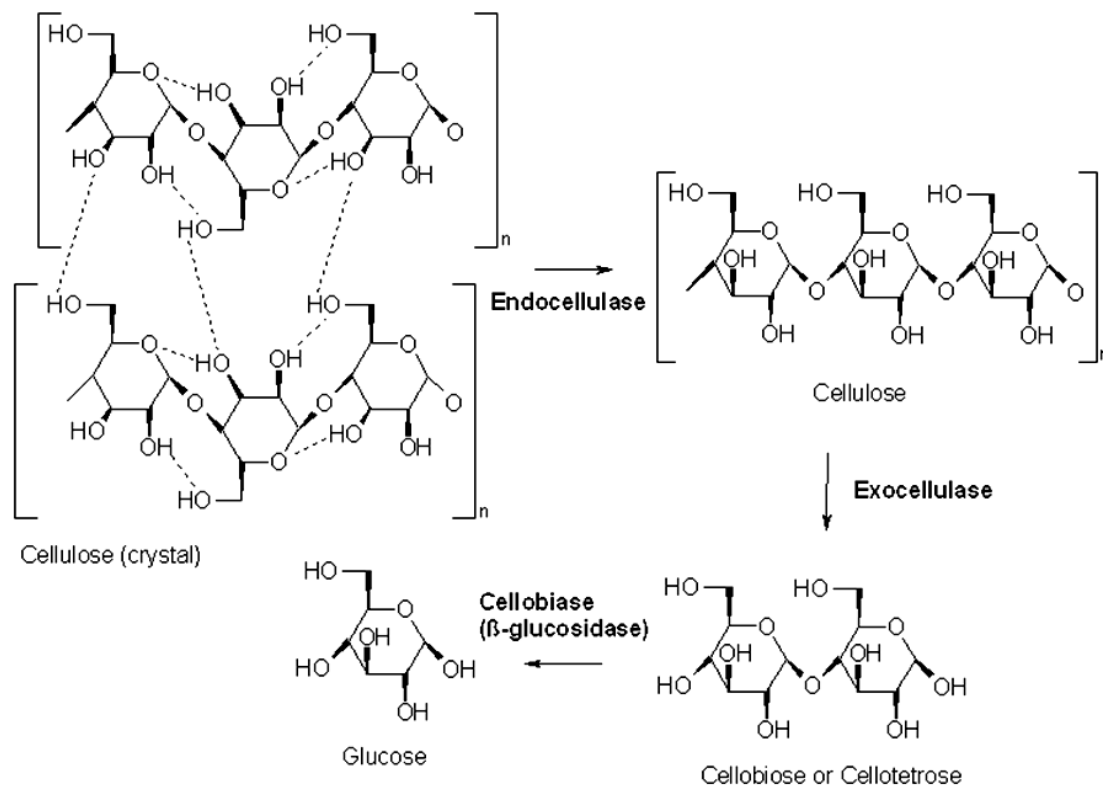


Fig. 3. Endocellulase, exocellulase and cellobiase.

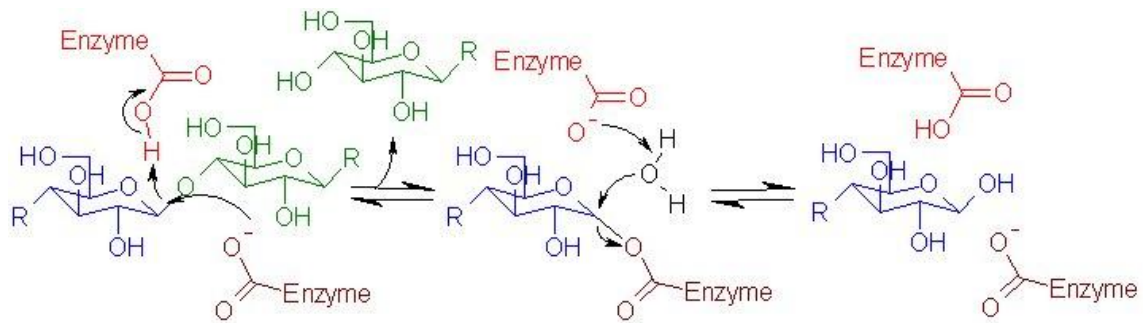
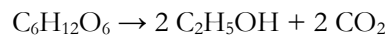


Fig. 4. Glycosidic bond in cellulose is hydrolyzed by cellulase enzymes.

Once the sugars have been separated from the residues such as lignin, they can be fermented. A wide range of sugars are available in lignocellulosic biomass and the ability to ferment a range of sugars is important in choosing the fermenting microorganisms. Xylose and arabinose are two sugars from the hemicellulose portion of lignocellulose. Since enzymes are generally substrate specific, the microorganisms used must have the essential enzymes that can act on these sugars and not just glucose. Yeast cells are now bioengineered to efficiently utilize xylose and arabinose, making them an attractive choice as fermenting microorganisms [8]. The overall equation for the fermentation of glucose is as follows.



The fermentation of other sugars is governed by similar equations, with the production of alcohol and carbon dioxide.

Next water has to be removed from the dilute ethanol solution in order for it to be used as fuel. Most of this removal is achieved through distillation. However, the purity achieved by this method is limited to around 95% due to the presence of water-ethanol azeotrope. The remaining water is removed by dehydration. Earlier methods of dehydration involved azeotropic distillation. It is a specific technique of adding another component to generate a new, lower-boiling azeotrope that is heterogeneous. It is similar to extractive distillation.

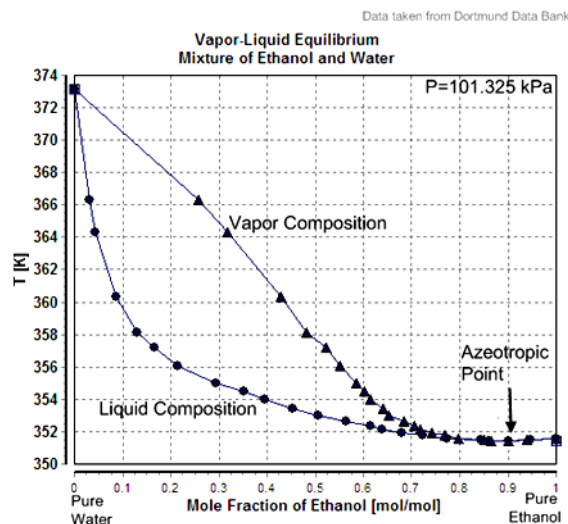
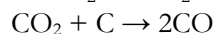
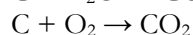
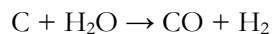


Fig. 5. Water-ethanol azeotropic point.

In contrast, the latest dehydration method involves the use of molecular sieves – typically zeolites. This physical method removes water from the water-ethanol mixture by adsorption as the mixed vapor passes through the bed of molecular sieve beads. Ethanol is first distilled to 96%, and then passed over a molecular sieve which adsorbs water from the vapor mixture. The concentration of ethanol is now above 96% and can be further distilled to obtain essentially pure ethanol. The spent molecular sieve is heated to

remove the adsorbed water and reused. The bed can also be regenerated by vacuum or by passing an inert gas or carbon dioxide.

Gasification is a thermochemical approach, in which biomass is simply used to produce synthesis gas (syngas) through partial combustion [9]. Biomass is first reduced to carbon (char) by pyrolysis, followed by alternating blasts of steam and air. Syngas is generated roughly according to the following equations.



The first reaction above is endothermic. Initially, steam is passed through the mixture as the first reaction proceeds. Temperature eventually falls to a point where there is not much reaction. Air is now passed through the mixture to encourage reactions 2 and 3. Reaction 2 is exothermic while reaction 3 is endothermic; on the overall, the two combined reactions to produce carbon monoxide are exothermic. The temperature rises up to a point where reaction 1 can be restarted. This cycle continues until all carbon is consumed.

Syngas can also be produced through catalytic partial oxidation. The University of Minnesota developed a metal catalyst that reduces the biomass reaction time by up to a factor of 100 [10]. The catalyst can be operated on the char at atmospheric pressure. The entire process is autothermic and therefore heating is not required.

The obtained syngas can then be led to a fermenter where bacteria take in carbon monoxide, carbon dioxide and hydrogen and produce ethanol and water [5, 11]. Organisms capable of metabolizing CO are extracted from hot springs, such as Carboxydocella sporoproducens isolated from a thermal spring of the volcanic Karymskoe Lake [12]. The ethanol produced then goes through a similar distillation and dehydration process as the biological approach. Alternatively, syngas can be fed to a catalytic reactor and ethanol is produced by a thermochemical process [13]. An ideal catalyst is rhodium-based which shows high selectivity. However, rhodium is expensive and research is now geared towards the less expensive copper-based catalysts. The disadvantage of copper-based catalysts is the need for promoters to suppress undesired reactions in order to maximise selectivity and minimise undesired by-products which uses up syngas unnecessarily. The general flow of material is illustrated in the following figure.

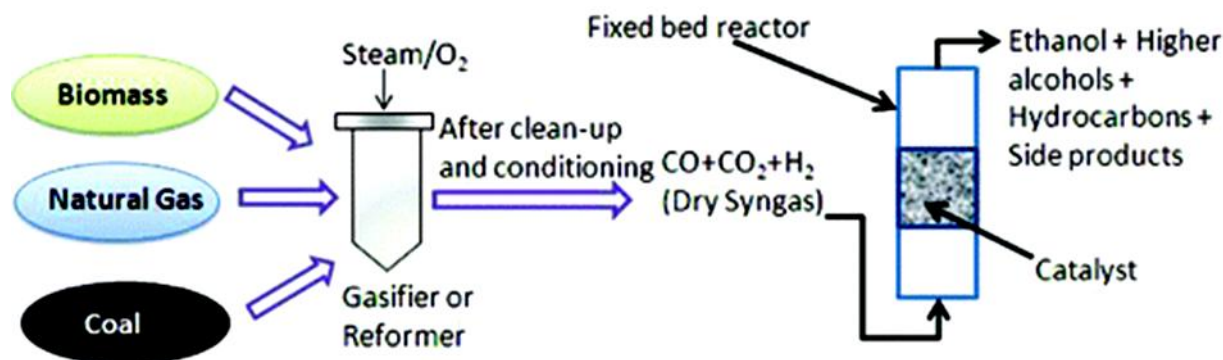


Fig. 6. Catalytic ethanol production from syngas.

As comparison, the syngas fermentation process has several advantages over the syngas thermochemical process since the former takes place at lower temperature and pressure, has higher reaction specificity, tolerates higher amounts of sulfur compounds, and does not require a strict ratio of CO to H₂. On the other hand, the former does have limitations such as: gas-liquid mass transfer limitation and low volumetric productivity. Nevertheless, bioengineering and chemical engineering could bring about important breakthroughs in this area.

As for the disadvantage of fermenting dissolved sugars, it is the presence of by-products. In syngas fermentation, a major by-product is hydrogen gas which is useful and easy to separate from the aqueous mixture. In the case of sugar-fermenting bacteria, redox reactions involving ATP and reducing equivalents are more or less determined in fixed ratios. Metabolic engineering of these organisms to produce specific

compounds will inevitably result in by-products in order to satisfy the redox balance. These by-products are most likely liquid and require additional separation to purify the product. Another advantage of using syngas over dissolved sugars as feedstock is that the use of a gaseous substrate allows the uncoupling of the hydraulic retention time from the substrate supply. This offers good possibility to control substrate inhibition and product formation.

Future Trend of Development

Combining Hydrolysis and Fermentation

Bacteria involved in the fermentation process have recently been genetically engineered to carry out hydrolysis as well. This means that cellulose can be directly converted to ethanol without breaking it down into simpler sugars. The process currently produces other metabolic waste products such as acetate and lactate, which lowers the pH of the mixture, thereby inhibiting microorganism activity and limiting the efficiency. Further improvement is still necessary.

Ethanol Production by Algae

Algenol is a research company that has enhanced certain strains of algae to make sugar and, through their enzymes, convert the sugar to ethanol [14]. The process produces ethanol in a gaseous form and is collected from the bioreactor and condensed as a liquid. This system is claimed to be able to produce 6000 gallons of ethanol per acre per year. Compared to corn's 370 gallons per acre per year or sugar cane's 890 gallons per acre per year, this is a great improvement in yield. The issue with implementing this technology would lie with Life Cycle Analysis to confirm whether this process actually has a smaller carbon footprint than alternative technologies such as electric vehicles. Electric vehicles are already actively adopted by many car manufacturers and existing technology can produce electricity cheaply and transmitted efficiently to charge electric cars. In the production of ethanol via algae, large amount of investment is still required to make the process economically viable. Even so, the investments are risky and may not give a better or even comparable return as compared to simply investing in existing electric technology. However, this can still change as global oil prices fluctuate and may increase to a point where ethanol from algae may be economically profitable.

By the way, in the USA approximately 0.5 trillion cubic feet of natural gas per year is used to produce ethanol [15]. Due to the discovery of huge reserves of shale gas which leads to a dramatic drop in natural gas prices, the economic advantage of this methane-derived syngas approach to produce fossil-derived ethanol is expected to increase in the near future.

Conclusions

Two methods of cellulosic ethanol production were discussed in detail. Innovative research on the use of algae for ethanol production is also being carried out. With these progresses, it is possible that the use of bioethanol may gradually increase to a level comparable to fossil fuels.

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