

Cellulosic Ethanol Production: Status of Conversion Technologies in the United States

Puneet Dwivedi^{*1}, Dr. Janaki R.R. Alavalapati², Pankaj Lal³

Summary. Reliance on foreign energy sources and rising greenhouse gases have compelled policy makers to promote cellulosic feedstock for ethanol production. This study evaluates the existing technologies which are available for converting cellulosic biomass into ethanol. Details of existing conversion technologies have been discussed. Additionally, the present adoption status of different technologies and the economics of cellulosic ethanol production have also been discussed. Emerging conversion technologies have also been characterized. It is expected that the review will be helpful in efficient allocation of resources for future technology development and in streamlining the whole initiative of cellulosic ethanol production.

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¹Room # 374, Newins Ziegler Hall
School of Forest Resources and Conservation
University of Florida, Gainesville, Florida (32611-0410)
Phone: +01-352-846-0902
Fax: +01-352-846-1277
Email: puneetdwivedi@gmail.com

* Corresponding Author

² Department of Forestry
College of Natural Resources
Virginia Tech, Blacksburg, VA (24061)
Phone: +01-540-231-5676
Fax: +01-540-231-3698
Email: jrra@vt.edu

³ Room # 374, Newins Ziegler Hall
School of Forest Resources and Conservation
University of Florida, Gainesville, Florida (32611-0410)
Phone: +01-352-846-0902
Fax: +01-352-846-1277
Email: pankajlal@ufl.edu

Introduction

The United States (U.S.) is the largest consumer of petroleum products in the world and is heavily dependent on imports for meeting the national demand of different petroleum products. For example, the U.S. consumed about 20.7 million barrels/day of petroleum products in 2007, out of which about 58% i.e. 12 million barrels/day was imported (EIA 2008a). Simultaneously, the use of gasoline for meeting transportation needs is continuously increasing in the country (Figure 1). It is predicted that the gasoline consumption will further rise along with the rising population, as it is the primary energy source for meeting the non-commercial transportation demand (EIA 2008b). Due to the increased use of petroleum products like gasoline, the amount of greenhouse gases released into the atmosphere, especially carbon dioxide (CO₂), has also shown a rising trend (Figure 1) (EIA 2008c). It was found that the transportation sector alone emitted about 34% of the total CO₂ released into the atmosphere in 2005 (EIA 2008d).

Figure 1: Gasoline consumption and CO₂ emissions in the United States

As a consequence of rising energy dependency, increasing emissions of greenhouse gases, and risks associated with the price fluctuations in the international energy markets, federal and various state governments have started to evolve new energy strategies in which the role of energy obtained from various renewable energy sources is emphasized. Out of many renewable energy resources (biomass, solar, wind, geothermal, tidal etc), biomass is given a high priority as it is the only source which can be directly utilized for production of various alternative transportation fuels, especially ethanol.

Using agricultural biomass for ethanol production raises concerns of food security (Mitchell 2008) and environmental degradation (Pimentel and Patzek 2005). Therefore, majority of the energy importing countries (including U.S.) are interested in utilizing cellulosic biomass as a feedstock for ethanol production. As the U.S. has a large cellulosic biomass production base (Perlack et al. 2005), production of ethanol from cellulosic feedstock and utilizing it as a substitute for gasoline could help in promoting rural development, reducing greenhouse gases, and achieving energy independence. Therefore, the federal government has announced various policy targets and incentives to promote the production of cellulosic ethanol in the country. For example, the Energy Independence and Security Act (EISA) of 2007 sets a target of producing 21 billion gallons of biofuels from cellulosic feedstocks by 2022. Additionally, the recently enacted Farm Bill of 2008 provides a subsidy of \$1.01 on every gallon of cellulosic ethanol produced.

Several technologies have been proposed to convert different cellulosic feedstocks into ethanol. These technologies range from fermentation (Lin & Tanaka 2006) to gasification (Perkins et al. 2008). However, doubts exist among various stakeholders about the commercial viability of existing conversion technologies (Waltz 2008; Tan et al. 2008; Ruan et al. 2008; Wright & Brown 2007). As a result, federal and various state governments are providing continuous funding support to several private companies and public institutions for developing and demonstrating a technology that can economically convert various cellulosic feedstocks into ethanol¹. It is expected that the successful demonstration of at least one conversion technology on a large scale will help in increasing the confidence of investors in cellulosic ethanol production process and in shifting the industry towards self reliance.

In light of the importance given to the development of a commercially viable conversion technology, it is essential to review the existing conversion technologies to ascertain their performance in terms of adoption rates and economics. Emerging technological alternatives should also be analyzed to better understand the future trajectory of technology development. Such an attempt will help in creating a baseline for the emerging conversion technologies and in guiding policy makers to streamline funding and institutional support.

In the next section of the paper, the composition of cellulosic feedstock is briefly discussed. In the third section, two major conversion technologies or base technologies that are commonly used for converting cellulosic feedstocks into ethanol, namely *hydrolysis* and *thermochemical*, are explained. An attempt has also been made to capture the different existing versions of both the base technologies. In the fourth section, the adoption status of existing conversion technologies is discussed. In the fifth section, economics in terms of ethanol production cost of the existing conversion technologies is discussed. In the sixth section, new trends in the technology development and alternate uses of cellulosic biomass are discussed and finally in the seventh section, the study is concluded.

Cellulosic feedstock composition

It is important to understand the cellulosic feedstock structure before it can be processed for ethanol production. Cellulosic feedstock is composed of lignin, cellulose, hemicellulose, and solvent extractives. Lignin acts as a cementing material and binds all other constituents together. It is also responsible for providing structural rigidity to a cellulosic feedstock. Cellulose is a polymer of repeating β -D-glucopyranose units and is a chief constituent of the feedstock. Hemicellulose is another constituent of the feedstock that is, like cellulose, a polysaccharide but less complex and easily hydrolysable. Soluble materials or extractives in the feedstock consist of those components that are soluble in neutral organic solvents. The distribution range of different constituents in softwood and hardwood is explained in Table 1 (Anonymous 2008; Miller 1999). Refer to Kuhad & Singh (1993) and Olsson & Hagerdal (1996) for information on constituents of other cellulosic feedstocks.

Table 1: Distribution range of wood components

Sugar present in the cellulose is mostly glucose. However, hemicellulose is a mixture of different types of sugars. It contains both C6 (glucose, mannose, and galactose) and C5 (xylose, arabinose, and rhamnose) sugars. Glucose, mannose, and xylose constitute about 95-97% of the total sugars. For example, distribution of sugars in loblolly pine (*Pinus taeda*), a commercial pine species of the southern U.S., is shown in Table 2 (Frederick et al. 2008a). It is to be noted that, being a biological compound, the feedstock is mostly comprised of three basic elements i.e. carbon, oxygen, and hydrogen. Different combinations of these elements are basic constituents of different feedstock components i.e. cellulose, hemicellulose, lignin, etc.

Table 2: Chemical constituents of loblolly pine (%)

Base Technologies

At present, several technologies are in use for converting cellulosic feedstocks into ethanol. However, all the existing technologies can be grouped into two broad categories namely *hydrolysis* and *thermochemical*. In hydrolysis, the polysaccharides (cellulose and hemicellulose) present in a feedstock are broken down to free sugar molecules (glucose, mannose, galactose, xylose, arabinose)². These free sugar molecules are then fermented to produce ethanol. As lignin cannot be used for ethanol production, it is removed during the conversion process and is generally utilized for meeting electricity or heat requirements of the ethanol mill³. In thermochemical based technologies, the feedstock is gasified entirely followed by either fermentation or catalytic conversion of the synthetic gas or syngas produced during gasification⁴. Production of ethanol through thermochemical route is independent of the sugar quantities originally present in the feedstock.

Details of specific technologies under each broad category of conversion technology i.e. hydrolysis and gasification are discussed below.

Hydrolysis technology

Hemicellulose and lignin present in the feedstock provide a protective covering to the cellulose. This protective cover should be altered for ensuring efficient hydrolysis. Moreover, cellulose has a crystalline structure, which makes it attack resistant and insoluble. Therefore, special provisions are needed to loosen the feedstock structure completely before undertaking cellulose hydrolysis. Figure 2 explains the basic steps generally undertaken while converting cellulosic feedstocks to ethanol through hydrolysis. During feedstock preparation, feedstock is first washed to remove dust and any other impurities. Then, feedstock is chipped or milled to increase the surface area so that chemicals/enzymes used in the subsequent steps can easily penetrate the structure. In the pretreatment process (also called first stage hydrolysis)⁵, hemicellulose is hydrolyzed into the basic sugars (xylose, mannose, arabinose, and galactose). A small amount of cellulose is also hydrolyzed to glucose during the pretreatment. The mixture obtained at the pretreatment is separated into liquid and solid (lignin + unhydrolyzed cellulose). The liquid is filtered and sent to a fermentation column for ethanol production. Solids are sent for another round of hydrolysis (also called second stage hydrolysis). After hydrolysis, cellulose is converted into glucose. Again, the mixture obtained at the end of hydrolysis is separated into liquid and solid (lignin). After filtration, liquid is sent to a fermentation column for ethanol production and lignin is fed into a boiler for heat production. Different types of microbes are needed for fermenting sugars obtained from cellulose and hemicellulose to ethanol. After fermentation is over, the mixture of ethanol and water is distilled to separate ethanol. Ethanol is then dehydrated to produce fuel grade ethanol (< 1% of water). Water produced as a part of distillation is diverted towards a wastewater treatment facility. The ethanol obtained is then transported for consumption purposes.

Figure 2: Schematic diagram of hydrolysis based cellulosic ethanol production

Currently, several versions of hydrolysis technology exist though the basic framework remains the same. Each version is distinguished from another depending upon the type of inputs used for hydrolyzing hemicellulose and cellulose into basic sugars. First, different techniques used for feedstock pretreatment (first stage of hydrolysis) are discussed followed by techniques which are commonly used for second stage of hydrolysis.

Pretreatment methods (first stage hydrolysis)

Thermal pretreatment

In thermal pretreatment, feedstock is heated to about 150-180°C to break down the hemicellulose and lignin. At higher temperatures (above 250°C), phenolic compounds are formed which later retard the fermentation process so care is taken not to pretreat the feedstock in severe thermal conditions (Ramos 2003). Four processes are commonly used for accomplishing thermal pretreatment i.e. steam pretreatment/steam explosion, liquid hot water, ammonia fiber explosion, and CO₂ explosion. During steam pretreatment, the feedstock is put in a large vessel and then steamed at a high temperature (up to 240°C) and pressure for few minutes. After a set time, the steam is released and the biomass is quickly cooled down. The difference between steam pretreatment and steam explosion pretreatment is the quick depressurization and cooling down of the biomass at the end of the steam explosion pretreatment which causes the water in the biomass to explode (Hendriks & Zeeman 2009; Jeoh 1998). In liquid hot water pretreatment, hot water is added to the feedstock in a slightly acidic environment to solubilize hemicellulose and prevent formation of any inhibitory compounds (Yang & Wyman 2004). In ammonia fiber explosion, processed feedstock is exposed to liquid ammonia at high temperature/pressure for small time and then the pressure is swiftly reduced. In a typical procedure, the dosage of liquid ammonia is 1-2 kg ammonia/kg dry biomass, temperature is 90°C, and residence time is about 30 minutes (Sun & Cheng 2002). Similar to steam and ammonia explosion pretreatment, CO₂ explosion is also used for pretreatment of processed feedstock. It was found that CO₂ explosion is more cost effective than ammonia explosion and did not cause the formation of inhibitory compounds (Zheng et al. 1998).

Acid pretreatment

In acid pretreatment, dilute sulfuric acid is added to the feedstock to hydrolyze hemicellulose (0.5-1.5%, temperature is greater than 160°C). Sometimes, concentrated sulfuric acid is also utilized for feedstock pretreatment but care should be taken as this might lead to the formation of fermentation inhibitory phenolic compounds. Moreover, the acid must be removed or neutralized before fermentation. Generally lime is used for neutralizing the medium and therefore gypsum is produced following the reaction. Dilute acid pretreatment is the most preferred method for feedstock pretreatment. Recently, nitric acid has also shown positive results in terms of better yields and solubility of lignin (Xiao & Clarkson 1997).

Alkaline pretreatment

Alkaline pretreatment uses bases like sodium hydroxide or calcium hydroxide. All lignin and part of the hemicellulose are removed, and the reactivity of cellulose for later hydrolysis is sufficiently increased. Alkaline-based methods are generally more effective at solubilising a greater fraction of lignin while leaving behind much of the hemicellulose in an insoluble polymeric form (Hamelinck et al. 2005; Mosier et al. 2005).

Oxidative pretreatment

In oxidative pretreatment, oxidatives like peracetic acid or hydrogen peroxide are used over the feedstock suspended in the water (Gould 1984). It was found that use of peracetic acid at the ambient temperature increased the ethanol yields to about 98% at a 21% peracetic acid pretreatment (Teixeira et al. 1999).

Organosolve pretreatment

In the organosolve process, an organic or aqueous organic solvent mixture with inorganic acid catalysts (hydrochloric acid or sulfuric acid) is used to break the internal lignin and hemicellulose bonds (Sun & Cheng 2002). The organic solvents used in the process include methanol, ethanol, acetone, ethylene, glycol, triethylene glycol, and tetrahydrofurfuryl alcohol (Chum et al. 1988; Thring et al. 1990).

Biological pretreatment

Brown-, white-, and soft-rot fungi are normally used for degrading lignin and hemicellulose present in the feedstock. Recently, Lee et al. (2007) have evaluated the pretreatment effects of three white rot fungi (*Ceriporia lacerata*, *Stereum hirsutum*, and *Polyporus brumalis*) on the Japanese red pine (*Pinus densiflora*). Similarly, Zhang et al. (2007) found that biological pretreatment with white rot fungi has potential for improving enzymatic hydrolysis of wood and grass. They found that fermentable sugar yield of bamboo culms (*Phyllostachys pubescence*) pretreated with two fungi (*Echinodontium taxodii* 2538 and *Trametes versicolor* G20) increased with increasing pretreatment time.

Hydrolysis technologies (second stage hydrolysis)

Acid hydrolysis

Acid hydrolysis is only applicable when feedstock has been pretreated according to the dilute acid process. Both dilute and concentrated acid options are available for hydrolyzing pretreated feedstock. At this stage, higher temperature (about 215°C) and dilute acid (4%) are used for converting cellulose to glucose. The concentrated acid process has a very high sugar yield (90%), can handle diverse feedstock, is relatively rapid (10-12 hours in total), and causes small degradation. However, the equipment required is more expensive when compared to dilute acid hydrolysis (Hamelinck et al. 2005).

Enzymatic hydrolysis

Enzymatic hydrolysis provides many advantages over acid hydrolysis. For example, enzymatic hydrolysis takes place at mild conditions of temperature and pressure. As a result glucose yields are high, chances of fermentation inhibiting compounds are less, equipment requirements are not significant, and

there is a reduction in the total environmental load of the whole process. Cellulases⁶ are usually a mixture of several enzymes. At least three major groups of cellulases are involved in the hydrolysis process: a) endoglucanase (EG, endo-1,4-D-glucanohydrolase, or EC 3.2.1.4) which attacks regions of low crystallinity in the cellulose fiber, creating free chain-ends; b) exoglucanase or cellobiohydrolase (CBH, 1,4- β -D-glucan cellobiohydrolase, or EC 3.2.1.91.) which degrades the molecule further by removing cellobiose units from the free chain- ends; c) β -glucosidase (EC 3.2.1.21) which hydrolyzes cellobiose to produce glucose (Coughlan & Ljungdahl 1988; Sun & Cheng 2002).

Fermentation

During fermentation, both C5 and C6 sugars are fermented to ethanol under anaerobic/aerobic conditions. Historically, yeast (*Saccharomyces cerevisiae*) was used to ferment C6 sugars i.e. glucose. Similarly, other microbes like *Zymomonas mobilis* have also been used. Other engineered microbes like *Escherichia coli* have also been developed which can ferment both C6 and C5 sugars.

Based on the different combinations of technologies adopted at the pretreatment, hydrolysis, and fermentation stages of ethanol synthesis, several integrated technologies have been developed. Also, few new integrated technologies have also evolved recently due to the developments in the area of biotechnology. In the section below, existing conversion technologies are discussed.

Integrated technologies based on hydrolysis

Simultaneous saccharification and fermentation

In simultaneous saccharification and fermentation, the feedstock is pretreated by dilute acid (1.1% sulfuric acid at 160°C for 10 minutes) to hydrolyze hemicellulose into sugars. The liquor is vented from the system and then neutralized using lime. Then, liquor containing C5 sugars is sent for the fermentation. Remaining solids contain cellulose and lignin. Yeast and enzymes are then added to the remaining solids where the enzymes digest cellulose to produce glucose. Yeast and other microbes ferment glucose to produce ethanol separately (Krishna et al. 2001).

Simultaneous saccharification and co-fermentation

In simultaneous saccharification and co-fermentation, the pretreated feedstock is exposed to different enzymes/microbes which not only hydrolyze cellulose and hemicelluloses into different sugars but also ferment sugars into ethanol. This technology is better than the simultaneous saccharification and fermentation technology in terms of cost effectiveness, better yields, and shorter processing time (Wright 1988; Chandel et al. 2007).

Two stage dilute sulfuric acid hydrolysis

Kadam (2000) has described the details of two-stage dilute sulfuric acid hydrolysis. In this type of hydrolysis, dilute sulfuric acid is used at pretreatment phase to hydrolyze hemicellulose. In the hydrolysis stage of the process, concentrated sulfuric acid is utilized for hydrolyzing cellulose. After hydrolysis is finished in both the stages, the liquid is separated, filtered and then neutralized (using lime) before it is sent for fermentation. Fermentation is conducted in steps. First, glucose is fermented to ethanol by the yeast *Sacromyces cerevisiae*. The mixture is then distilled to remove the unconverted xylose. Then a second yeast, *Pachysolen tannophilus*, which ferments xylose to ethanol is added to the remaining solution. Ethanol produced from xylose is then distilled (Shleser 1994).

Biomass fractionation

In biomass fractionation, feedstock is pretreated using the steam explosion method. Then, resulting mass is washed by either water or alkali to separate out the components of the biomass i.e. hemicellulose, cellulose, and lignin (Glasser & Wright 1998). Once separated, components containing sugars are further hydrolyzed to produce sugars. Sugars produced are fermented to obtain ethanol.

Recently, a new technique has been developed using which cellulosic biomass is fractionated in a very small amount of time (Guffey & Wingerson 2002).

Thermochemical technology

In thermochemical conversion, constituents of feedstock are first converted into syngas (a mixture of carbon monoxide, hydrogen, CO₂, methane, and nitrogen) under intense heat and partial supply of air inside a gasifier. Different types of gasifiers are available in the market. However, performance of fluidized-bed gasifier has been found most satisfactory in gasifying different types of feedstocks. The syngas, so produced after gasification, is then either fermented or catalytically converted to ethanol. Figure 3 shows the schematic diagram of ethanol formation through thermochemical route. Details of both the technologies i.e. fermentation-based and catalyst-based are briefly discussed below.

Figure 3: Schematic diagram of ethanol production through gasification technology

Gasification-fermentation based ethanol production

The feedstock is washed to remove any impurities and then chipped to the required size. Then, chips are dried to attain a desired moisture level (5-20% by weight). Sand bed present inside a fluidized bed gasifier is preheated to a temperature of about 550°C using an external fuel supply. Once optimum temperature is achieved, feedstock is fed into the bed. On coming in contact with hot sand, the feedstock decomposes producing syngas. The supply of air is simultaneously controlled for preventing complete combustion of feedstock and to raise the temperature of the sand bed to about 800°C. Once the optimum conditions are achieved, the gasifier can run on its own without any external supply of additional fuel. The syngas so produced is collected from the top of the gasifier. Gas is cleaned to remove tar and ash. Once cleaned, gas is cooled to the normal ambient temperature and stored at a high pressure. Cooled and cleaned gas is fed into an ethanol conversion chamber where microbes ferment the gas into ethanol and acetic acid. After fermentation is complete, the liquid is distilled to separate ethanol from other products. The ethanol produced is then dehydrated to produce fuel quality ethanol. Many microbes have been developed which can successfully ferment the syngas into required compounds like *Clostridium carboxidivorans* P7 (Liou et al. 2005), *Clostridium ljungdahlii*, and *Clostridium autoethanogenum* (Abrini et al. 1994; Vega et al. 1990). Rajagopalan et al. (2002) have found that fermentation of the syngas by the microbe (P7) is sensitive to the syngas constituents and syngas should be cleaned properly for ensuring effectiveness of the process. For example, Ahmed et al. (2006) found that presence of nitric oxide in the syngas (150 ppm) prevents fermentation of gas constituents by the P7.

Gasification-catalyst based ethanol production

In catalytic based ethanol production, all the processes remain the same until the gas enters into an ethanol conversion chamber. Before entering into the chamber, gas is heated to 300°C at a pressure of 69 bar. Gas is also mixed with water and methanol to improve the yield of higher alcohols. The mixture is passed through the synthetic catalyst (molybdenum-disulfide based) to obtain methanol, ethanol, and higher linear alcohols up to pentanol, water, methane, and minor amounts of other hydrocarbon byproducts. The chamber effluent is finally cooled to 43°C using cooling water, and excess syngas is diverted to the gas cleaning area. Obtained effluent is sent to distillation for ethanol recovery. Finally, the ethanol obtained is dehydrated to achieve a specified moisture level (Phillips 2007).

Adoption status of different technologies

Inspired by the initiatives of federal government in terms of several monetary subsidies, many private entrepreneurs have ventured into cellulosic ethanol production. Figure 4 shows the details of the total quantities of cellulosic ethanol expected to be produced within the country in coming years by employing different conversion technologies (RFA 2008).

Figure 4: Conversion technologies used for producing cellulosic ethanol

As observed from Figure 4, it is expected that about 243 million gallons of cellulosic ethanol will be produced by the end of 2012 and three conversion technologies (enzymatic hydrolysis; simultaneous saccharification and fermentation; and gasification catalytic conversion and distillation) will be majorly employed for converting various cellulosic feedstocks into ethanol⁷. Government has so far supported existing cellulosic ethanol mills through various grants and it is thought that the commercial viability of the cellulosic ethanol production will be proven to the private investors by the end of 2012 (Sandor et al. 2008). Additionally, many small scale ethanol mills are coming up at various places to test the efficacy of newly developed conversion technologies.

It was observed that the majority of cellulosic ethanol mills which are under construction have plans to meet their cellulosic feedstock supply either from the agriculture sector (corn stover, corn cob, wheat straw, rice straw, barely straw, switch grass, sugar cane) or from municipal solid wastes. Based on the current trend, it is expected that there will be few cellulosic ethanol mills which will be utilizing only forest biomass for producing ethanol in the future. However, forestry biomass available on nation's forestlands can play an important role in sufficing the future national cellulosic biomass demand as forestlands occupy about 749 million acres i.e. about 33% of the total geographical area of the U.S. (Smith et al. 2002). Furthermore, it was found that at the market price of <\$30/dry ton delivered, the total availability of forestry feedstocks will be about 24% of the total cellulosic biomass available in the nation (excluding wood obtained from urban areas but including forest mill residues, dedicated forestry crops, and forestry residues). However, at the market price of <\$40/dry ton delivered, total availability of forestry feedstocks will jump to 45% of the total availability of cellulosic feedstocks at the national level (Walsh et al. 2000). This implies that there exists a need for promoting construction of more forestry feedstock utilizing cellulosic ethanol mills so that the commercial viability of utilizing forestry feedstock for ethanol production can be proved. This will also help in diversifying the cellulosic feedstock base which is an essential requirement for achieving the target of EISA 2007.

Economics of the adopted technologies

Hydrolysis-based technologies

Production of ethanol from cellulosic feedstocks is costly when compared to its production from starch based agricultural feedstocks (McAloon et al. 2000). Therefore the goal of the federal government is to bring down the cost of production of cellulosic ethanol to \$1.33/gal by the end of 2012 by improving overall efficiency of conversion technologies. Sassner et al. (2008) have analyzed the cost effectiveness of three cellulosic feedstocks (salix, corn stover, and spruce) and they concluded that conversion technology used for ethanol production has more important implications for the cost-effectiveness of the conversion process than the type of feedstock used. Shleser (1994) compared the cost of ethanol produced using seven integrated technologies. Results of the study are summarized in Table 3.

Table 3: Ethanol plant performance summary, biomass cost included

Table 3 clearly shows that as the scale of the ethanol mill increases, the production cost of ethanol falls. Also, the production cost of the ethanol is directly related to the cost of biomass feedstock. It was

found that among all the conversion technologies, the production cost of ethanol was highest for the concentrated acid hydrolysis, neutralization and fermentation technology and lowest for simultaneous saccharification and fermentation technology. Recently, Huang et al. (2008) have stated that for an ethanol mill based on simultaneous saccharification and co-fermentation technology, the ethanol production cost decreases with increasing plant sizes in the range of 1,000 dry Mg/day to 4,000 dry Mg/day. It was also found that the cost of production of ethanol from hybrid poplar increases if the plant size is more than 4,000 dry Mg/day as feedstock costs rise faster than non-feedstock costs. They also estimated that the cost of ethanol production was not variable with the type of feedstock utilized i.e. corn stover, switch grass, hybrid poplar, and aspen wood.

So & Brown (1999) conducted a study in which they found that the cost of production of ethanol from a 25 million gallon/year ethanol plant was \$1.57/gal, \$1.28/gal, and \$1.35/gal respectively for fast pyrolysis integrated with a fermentation step, simultaneous saccharification and fermentation, and dilute sulfuric acid hydrolysis and fermentation. Wooley et al. (2002) have found that to minimize the production cost of ethanol produced using corn stover as a feedstock and co-current dilute acid prehydrolysis and enzymatic hydrolysis as a technology, emphasis should be on increasing the conversion efficiencies of hemicelluloses and cellulose to fermentable sugars. Hamelinck et al. (2005) echoed similar thoughts. They analyzed four technologies and three scenarios and found that with an increase in sugar conversion efficiencies, commercial production of cellulosic ethanol was feasible. Recently, for a 55 million gallons/year ethanol production facility, Aden (2008) conducted a study and found that the total selling price of ethanol is about \$2.43/gallon when simultaneous saccharification and fermentation technique is used for ethanol production. It was also noted that the selling price has shown continuous declining trends since 2001. Feedstock costs were found to be about 40% of the total selling price of ethanol. Feedstock costs have been found to be significant in determining the final cost of the ethanol especially when the conversion technology costs are falling at a faster pace (Bohlmann 2006). Leistritz et al. (2006) have analyzed the production cost of ethanol from wheat straw in North Dakota and estimated the production cost to be \$1.56/gal.

Thermochemical technologies

Phillips (2007) modeled cellulosic ethanol production through gasification technology and catalytic conversion. The minimum selling price was found to be \$1.07/gal based on the anticipated and achievable technology parameters by 2012. Tembo et al. (2003) noted that the breakeven cost for the ethanol produced using thermochemical-fermentation technology will be about \$0.76/gal. Recently, Piccolo & Bezzo (2008) have estimated that the cost of production of ethanol produced using gasification-fermentation based technology will be higher than that of the enzymatic hydrolysis technology. However, Wei et al. (2008) have found that the cost of ethanol produced using gasification-catalytic conversion technology will be lower than the unit cost of ethanol produced using hydrolysis fermentation as processing time is lowest in the former technology.

The economic analysis clearly reveals that the unit cost of ethanol production has fallen in recent years due to technological advancements and it is expected that the cost of producing ethanol from cellulosic feedstocks will become comparable to the ethanol derived from starch feedstocks in coming years. It was also observed that the scale of operations has an impact on the production cost of ethanol and an optimum size of an ethanol mill should be close to 4,000 dry Mg/day of feedstock consumption. Furthermore, the type of feedstock does not appear to be significant in determining the production cost of ethanol, compared to the conversion technology. It can be inferred that the future production cost of ethanol will be lowest for gasification-catalytic conversion followed by hydrolysis and then the gasification-fermentation technology. There also exists a need for reducing the cost of transporting feedstocks to the ethanol mill as feedstock costs are about 40% of the total production cost of ethanol at present and have not shown a significant declining trend.

Emerging developments

The importance given to the commercial viability of ethanol production from cellulosic feedstocks has attracted many scholars. It has been found that irrespective of the technology applied, the costs of the plant are correlated with the overall energy loss of the plant (Lange 2007). Therefore, many new ideas have been tried at different levels for ensuring commercial production of ethanol from cellulosic feedstocks by increasing either the overall efficiency of the plant or by reducing the major costs, especially the transportation costs of different feedstocks. Some of these emerging technologies are discussed below.

Consolidated bioprocessing

In consolidated bioprocessing, only one microbial community is employed both for the production of cellulases and fermentation, i.e. cellulose production, cellulose hydrolysis, and fermentation are carried out in a single step (Cardona & Sánchez 2007). Lynd et al. (2005) have elaborated two strategies for enabling consolidated bioprocessing. First, engineering naturally occurring cellulolytic microorganisms to improve product-related properties such as yield and titer and second, engineering non-cellulolytic organisms that exhibit high product yields and titers to express a heterologous cellulase system enabling cellulose utilization. They have estimated that consolidated bioprocessing has a potential to provide a lowest cost route for biological conversion of cellulosic biomass to fuels and other products in processes featuring hydrolysis by enzymes and/or microorganisms.

Mobile fast pyrolysis

Reducing transportation costs will help in ensuring economical production of cellulosic ethanol, as the cost of feedstock is about 40% of the final cost of produced ethanol. Because cellulosic biomass is a light density solid, it occupies a large volume resulting in increased transportation costs. One way to overcome this problem is to densify the feedstock at the harvest site and then transport it to the mill site for ethanol production (Li & Liu 2000; Petrolia 2008; Husain et al. 2002). Recently, establishment of mobile fast pyrolysis plants at the feedstock source for producing pyrolysis oil has been suggested as one potential solution. It is observed that the energy density of pyrolysis oil is about 6-7 times higher than the energy density of green whole tree chips at 45% and 56% moisture content respectively (Badger & Fransham 2006; Czernik & Bridgwater 2004). Pyrolysis oil can be gasified and syngas can be utilized for ethanol production. However, pyrolysis oil is very complex and unstable and therefore, there exists a need of advance technologies to utilize pyrolysis oil for ethanol production successfully.

Integrated ethanol refineries

Increasing the energy efficiency of the whole conversion process is key to ensuring the commercial viability of cellulose based ethanol production. Recently, Frederick et al. (2008b) took a holistic approach and analyzed the whole system of producing ethanol from loblolly pine and using the residual biomass as a fuel for a combined heat and power plant. They found that ethanol can be produced at \$1.29/gal based on a delivered wood cost of \$63.80/dry metric ton at 95% conversion efficiency of carbohydrates in wood to sugars for a 93 million gallons annual plant capacity. Frederick et al. (2008a) also analyzed the feasibility of ethanol production in a Kraft Paper mill. They found production cost of ethanol to be between \$1.33/gal and \$2.92/gal depending upon process conditions and selectivity of hemicelluloses removal. Leistritz et al. (2006) have also evaluated the integrated biorefinery concept in North Dakota and found that the production of cellulose nanowhiskers (CNW) would be an enhancement to the economic performance of a wheat straw to ethanol mill.

Alternate uses of cellulosic biomass- biopower

Biopower experienced a dramatic factor-of-three increase in grid-connected capacity after the Public Utilities Regulatory Policy Act (PURPA) of 1978 guaranteed small electricity producers (less than 80 MW) that utilities would purchase their surplus electricity at a price equal to the utilities' avoided cost

of producing electricity. In the period 1980-1990, growth resulted in industry investment of \$15 billion dollars and the creation of 66,000 jobs (Bain 2004). Even today, biopower plays a major role in total renewable electricity produced in the nation as about 16% electricity produced from renewable sources comes from biomass only (EIA 2008e). Recently, due to several incentives announced by federal government, the interest in using biomass for electricity production has gone up and many entrepreneurs are establishing new power plants which will utilize cellulosic feedstocks to produce electricity. For example, Gainesville Regional Utility will establish a 100MW power plant in Gainesville, Florida which will use various cellulosic feedstocks for electricity production. The use of biomass-based electricity has shown rising trend as indicated in Figure 5 (EIA 2008f). It is possible that the rise in number of such power plants will increase the competition for cellulosic biomass and can severely impact the availability of cellulosic biomass for ethanol production.

Figure 5: Consumption of biomass-based electricity (1985-2007)

Conclusions

Production of cellulosic ethanol presents a challenge in terms of development of a commercially viable conversion technology and with the rising interest it is expected that such a technology will soon be developed. However, it is more likely that the developed conversion technology will be based on the thermochemical platform rather than sugar platform as embedded technologies like gasification and catalytic conversion are already quite mature and only small improvements are needed to customize the present technology for ethanol production. Similarly, it is also expected that advances in reducing the feedstock costs will help in reducing the total cost of cellulosic ethanol production.

In terms of technology adoption, only three technologies have gained broader acceptance. It is essential to evaluate other technologies on a large scale for understanding their potential in meeting the objective of economical production of cellulosic ethanol. Considering the importance of forest biomass in meeting the cellulosic biomass demand of the nation in the near future, more ethanol mills based on different types of forest biomass should be established at several levels. This will help in understanding the exact nature of associated problems with the utilization of forest biomass as a feedstock for ethanol production.

Cellulosic ethanol holds the promise to supplement the growing energy needs of the nation. However, at the same time, it is important to strike a harmonious chord with the other natural processes that are associated with the production of cellulosic feedstocks. For example, in case of forestry feedstocks, it is important to evaluate the impacts of biomass production on the local biodiversity or on the local watershed. Similarly, in case of agricultural feedstocks, it is important to evaluate the impact on soil and water conservation and nutrient management of soils. Understanding these relationships will help in developing a comprehensive cellulosic feedstock based bioenergy development in the country.

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Figure 1: Gasoline consumption and CO₂ emissions in the United States

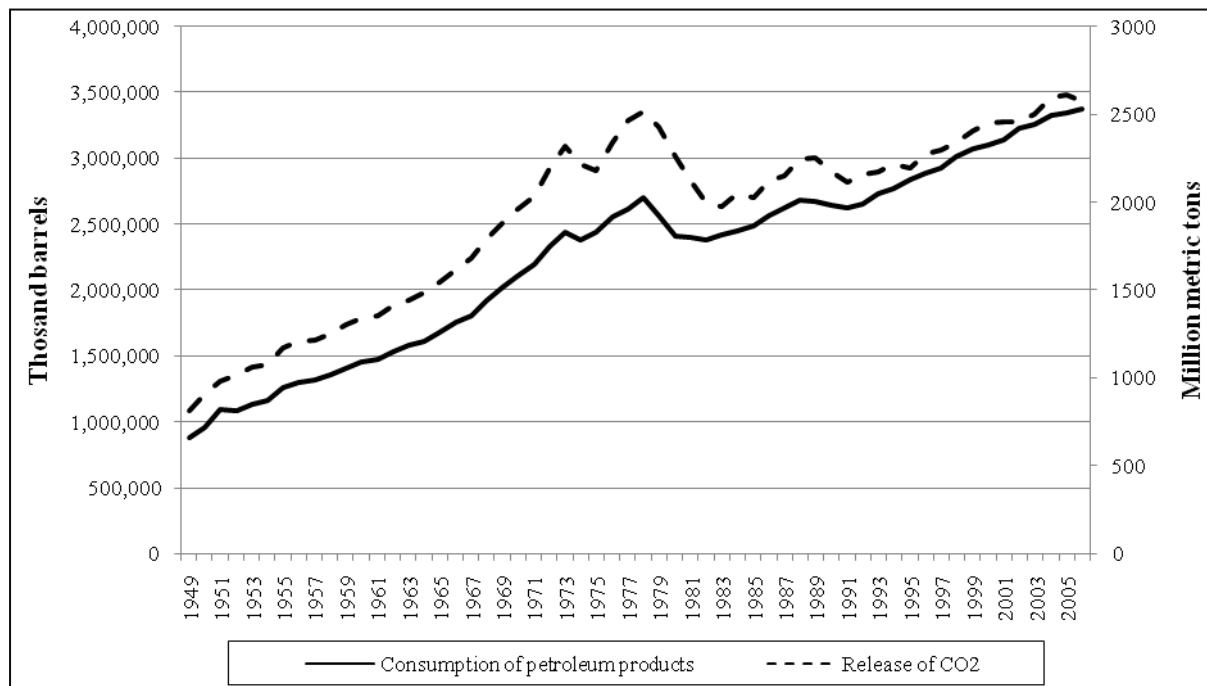


Figure 2: Schematic diagram of hydrolysis based cellulosic ethanol production technologies

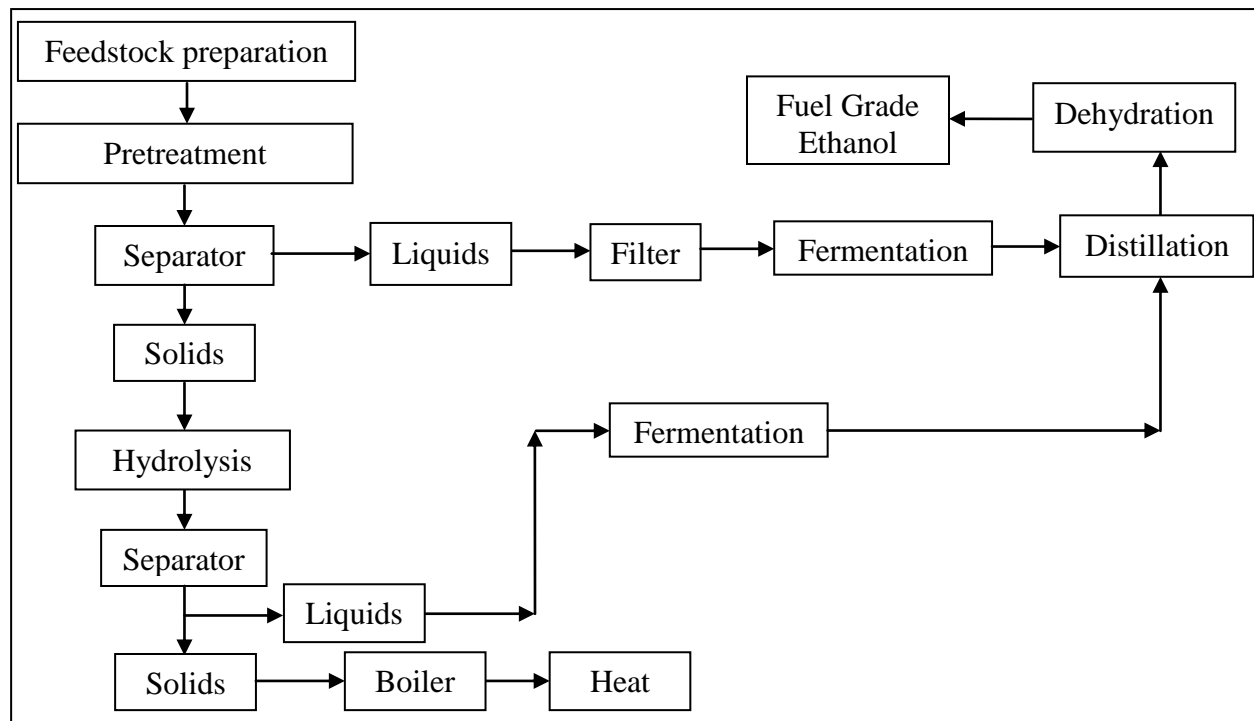


Figure 3: Schematic diagram of ethanol production through gasification technology

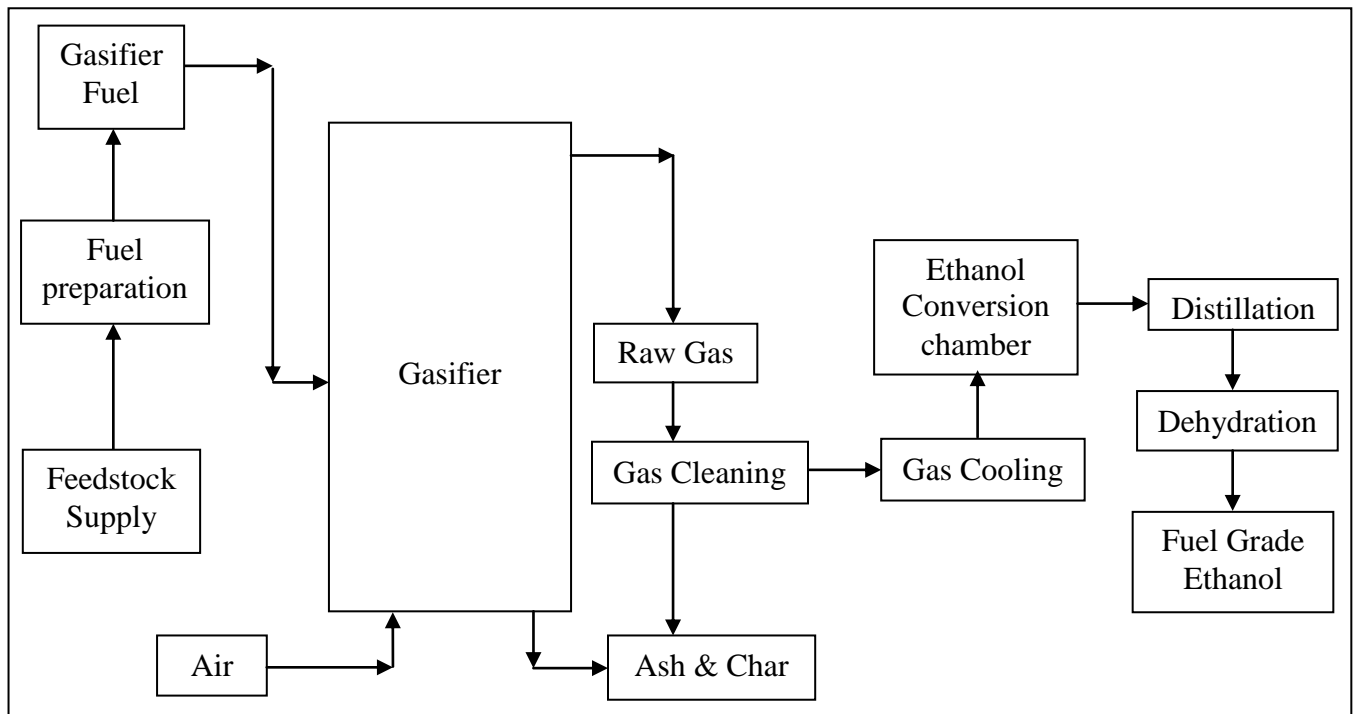


Figure 4: Conversion technologies used for producing cellulosic ethanol

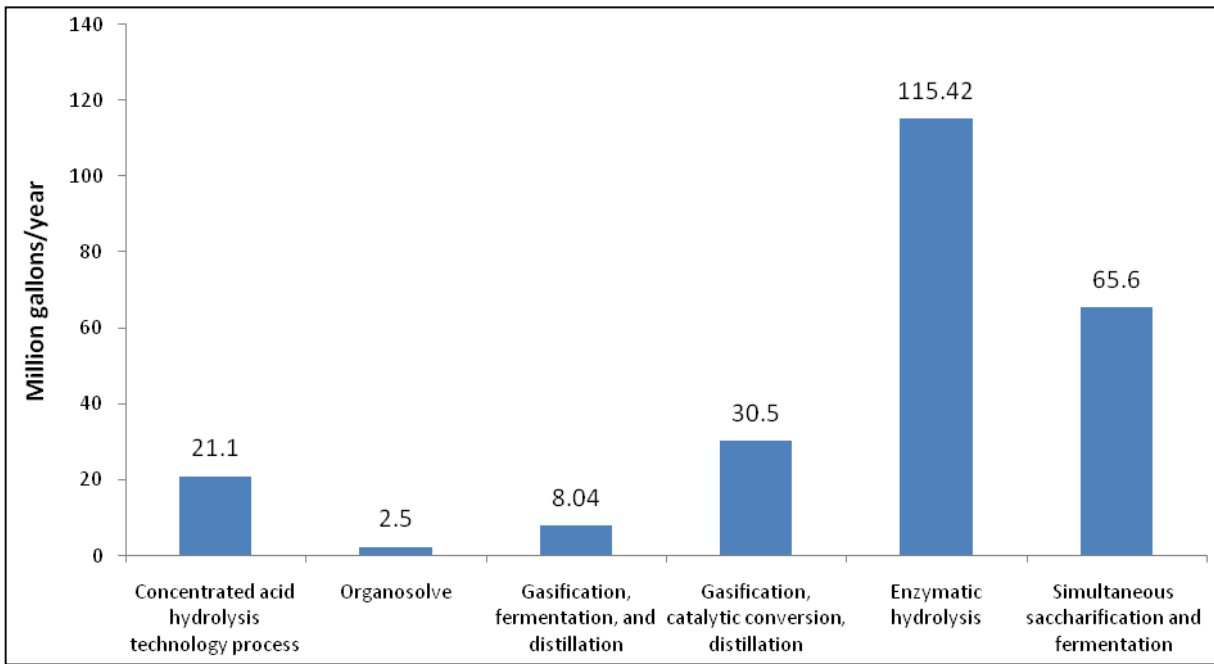


Figure 5: Consumption of biomass-based electricity (1985-2007)

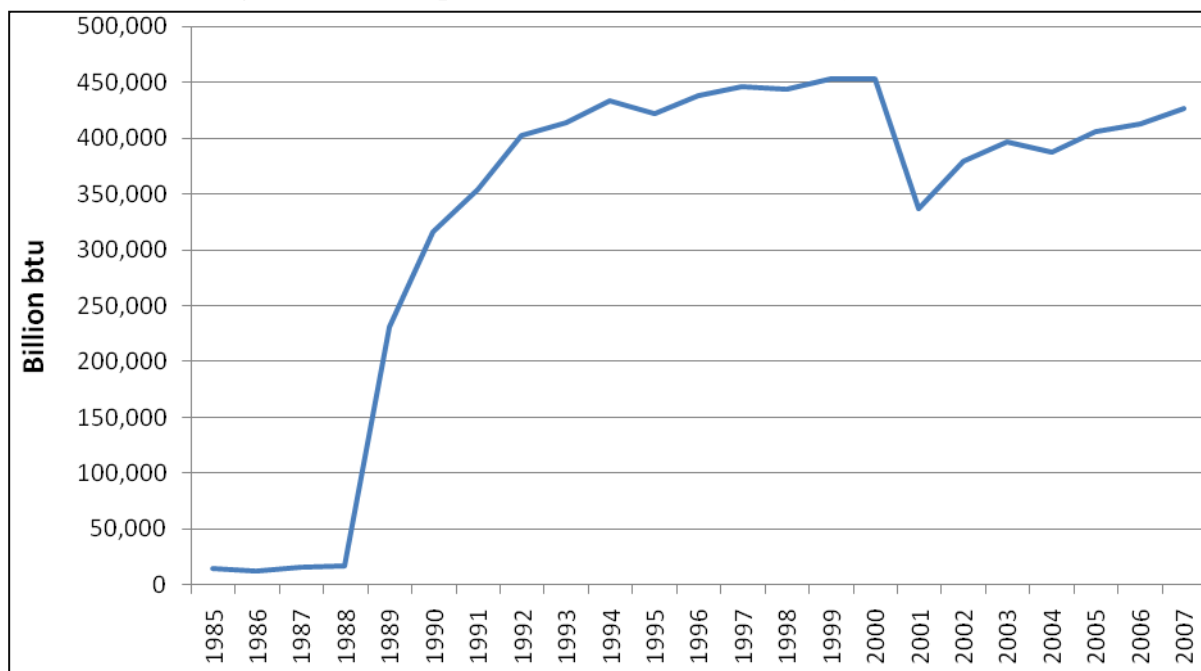


Table 1: Distribution range of wood components

| Wood Components | Hardwood (%) | Softwood (%) |
|------------------------|---------------------|---------------------|
| Cellulose | 40 - 50 | 40 - 50 |
| Hemicellulose | 25 - 35 | 25 - 30 |
| Lignin | 20 - 25 | 25 - 35 |
| Pectin | 1-2 | 1-2 |
| Starch | Trace | Trace |

Table 2: Chemical constituents of loblolly pine (%)

| Constituents | Percentage (%) |
|-------------------------------------|-----------------------|
| Cellulose (C6) | 43.6 |
| Hemicellulose convertible to sugars | |
| Mannan (C6) | 10.8 |
| Galactan (C6) | 2.2 |
| Xylan (C5) | 6.6 |
| Arabinan (C5) | 1.6 |
| Acetal | 1.1 |
| Uronic anhydride | 3.7 |
| Lignin | 26.8 |
| Extractives | 3.2 |
| Ash | 0.4 |
| Total | 100.0 |

Table 3: Ethanol plant performance summary, biomass cost included

| Process | Biomass cost: \$50/ton (dry matter) | | Biomass cost: \$108/ton (dry matter) | |
|---|--|---------------------------------|---|---------------------------------|
| | Ethanol (\$/gal) 25 Mgal/year | Ethanol (\$/gal) 5 Mgal/year | Ethanol (\$/gal) 25 Mgal/year | Ethanol (\$/gal) 5 Mgal/year |
| Simultaneous saccharification and fermentation | 1.48 | 1.88 | 2.11 | 2.51 |
| Concentrated acid hydrolysis, neutralization and fermentation | 2.28 | 2.76 | 3.01 | 3.49 |
| Ammonia disruption hydrolysis and fermentation | 1.81 | 2.40 | 2.48 | 3.06 |
| Steam disruption, hydrolysis and fermentation | 1.63 | 2.15 | 2.25 | 2.77 |
| Acid disruption and transgenic microorganism fermentation | 1.86 | 2.45 | 2.50 | 3.10 |
| Concentrated acid hydrolysis, acid recycle and fermentation | 1.86 | 2.19 | 2.50 | 2.83 |
| Acidified acetone extraction, hydrolysis and fermentation | 1.70 | 2.13 | 2.30 | 2.72 |

Footnotes

¹Already, federal government has provided a funding of \$1 billion for promoting research in developing a commercial viable conversion technology for producing cellulosic ethanol (Curtis, 2008)

²This process is also known as saccharification.

³Technologies which hydrolyze the sugars to produce ethanol are also known as sugar platform technologies

⁴Gasification is a process that uses heat, pressure, and steam to convert different materials including cellulosic biomass into syngas composed primarily of carbon monoxide and hydrogen (Rezaiyan and Cheremisinoff, 2005).

⁵Pretreatment also helps in loosening the wood structure completely. As a result, cellulose present in the wood becomes available for hydrolysis in subsequent step.

⁶Cellulase refers to a class of enzymes produced chiefly by fungi, bacteria, and protozoans that catalyze the hydrolysis of cellulose.

⁷These three conversion technologies will be utilized for producing about 83% of the total estimated cellulosic ethanol production in 2012.