FEEDSTOCK PRETREATMENT STRATEGIES FOR PRODUCING ETHANOL FROM WOOD, BARK, AND FOREST RESIDUES

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Energy and environmental issues are among the major concerns facing the global community today. Transportation fuel represents a large proportion of energy consumption, not only in the US, but also worldwide. As fossil fuel is being depleted, new substitutes are needed to provide energy. Ethanol, which has been produced mainly from the fermentation of corn starch in the US, has been regarded as one of the main liquid transportation fuels that can take the place of fossil fuel. However, limitations in the supply of starch are creating a need for different substrates. Forest biomass is believed to be one of the most abundant sources of sugars, although much research has been reported on herbaceous grass, agricultural residue, and municipal waste. The use of biomass sugars entails pretreatment to disrupt the lignin-carbohydrate complex and expose carbohydrates to enzymes. This paper reviews pretreatment technologies from the perspective of their potential use with wood, bark, and forest residues. Acetic acid catalysis is suggested for the first time to be used in steam explosion pretreatment. Its pretreatment economics, as well as that for ammonia fiber explosion pretreatment, is estimated. This analysis suggests that both are promising techniques worthy of further exploration or optimization for commercialization.

Keywords: Energy; Biomass; Pretreatment; Ethanol; Saccharification; Biorefinery; Steam explosion; Ammonia fiber explosion

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INTRODUCTION

Energy security and climate change imperatives require large-scale replacement of petroleum-based fuels, as well as improvement of vehicle efficiency (Farrell et al. 2006; Hahn-Hagerdal et al. 2006). Renewable fuels, such as bioethanol, are becoming increasingly important as a consequence of heightened concern for the greenhouse effect, depleting oil reserves, and rising oil prices (Ohgren et al. 2007). Fuel ethanol is mainly used as an oxygenated fuel additive. The higher octane number of the fuel mixture, when it contains ethanol, reduces the need for toxic, octane-enhancing additives such as methyl tertiary butyl ether. Due to the oxygen in ethanol molecules, there is also a reduction of carbon monoxide emission and non-combusted hydrocarbons. It is believed that ethanol is 15% more efficient than gasoline in optimized spark-ignition engines, while it has about the same overall transport efficiency as diesel in compression-ignition engines (Bailey 1996). It is also believed that a given volume of ethanol could provide energy enough to drive about 75~80% of the distance as the same amount of gasoline, although it has the only about two-thirds of the energy content (Galbe and Zacchi 2002). Table 1 shows the densities and low heating values of gasoline, diesel, and ethanol, respectively (US Department of Energy).

Table 1. Energy Content Comparison between Gasoline, Diesel and Ethanol (Data excerpted from the website of US department of energy: Anonymous)

	Density @ 60 ºF (lb/gal)	Energy(BTU/Gallon) LHV@60 ºF
Gasoline	6.0~6.5	116,090
No. 2 Diesel	7.079	129,050
Ethanol	6.61	76,330

Note: LHV=Low Heating Value

Most ethanol is currently produced by fermentation of either corn starch or sucrose. The United States, Brazil and China are in the top of countries that produce the largest quantities of fuel ethanol. If the oil crisis continues to develop, ethanol is one of the most promising biofuels that can be used to replace gasoline for tomorrow's transportation vehicles. Until recently, the high cost of ethanol production has been a factor retarding commericial use of ethanol and requiring subsidies to promote development. Reduction of the production cost would lead to a faster commercialization of economically feasible processes and would increase the competitiveness of ethanol with fossil fuels. The raw materials account for 40~70% of the total ethanol production costs based on current sugar- or starch-containing feedstocks, such as sugarcane and corn. Commercial feasibility is also dependent on production of animal feed as a by-product (Claassen et al. 1999; Sun and Cheng 2002b). Lignocellulosic biomass is believed to be less expensive and more plentiful than either starch- or sucrose-containing feedstocks. Lignocellulosic-based biofuels could replace about 30% of the petroleum currently consumed by the USA, if materials such as forest residues (e.g. sawdust, wood bark), agricultural residues (e.g. corn stover), and herbaceous grass (e.g. Switchgrass), as well as municipal waste, etc., are used (Galbe and Zacchi 2002; Gray et al. 2006; Mosier et al. 2005; Wyman et al. 2005). It has been estimated that more than one billion tons of such biomass can be made available annually in the USA (Perlack 2005). From the harvest and life cycle points of view, forest materials provide considerable advantages as an input to a biorefinery that might make fuels and chemicals. Extensive research has been exploring substrates from these different categories. Figure 1 summarizes some of the major lignocellulosics that have been investigated for bioethanol production.

Corn stover, wheat straw, and sugar bagasse are among the agricultural residues that have attracted the most interest of research. Other agricultural residues that have been explored include rice straw, rice hull, corncob, oat hull, and corn fiber, among others; these can be classified into a group derived from food crops. Research has also been performed on substrates such as cotton stalk and cotton gin; these can be classified as a group deriving its source from nonfood crops, as shown in Fig. 1 (Chang et al. 2001; Chen and Liu, 2007; Esteghlalian et al. 1997; Moniruzzaman et al. 1997; Rubio et al. 1998; Saha 2003; Saha et al. 2005; Sun and Chen 2007; van Walsum and Shi 2004). Switch grass and Bermuda grass have been the intensive substrates explored in the herbaceous grass category, while other substrates such as reed canarygrass and alfalfa fiber have also been studied in the same category (Chang et al. 2001; Dien et al. 2006). Some research has utilized municipal wastes as substrates and researched the conversion of these substrates into ethanol (Li et al. 2007; Lissens et al. 2004). A lot of work has been carried out to explore woody substrate to produce ethanol (Ballesteros et al. 2000; Berlin et al. 2007; Demirbas 2004, 2005, 2007, 2008). The woody substrates can be roughly classified into two classes, one is wood or wood chips while the other forest residues. In this review article, the substrates will be majorly focused on woody biomass as long as the discussion of pretreatment and economics are concerned.

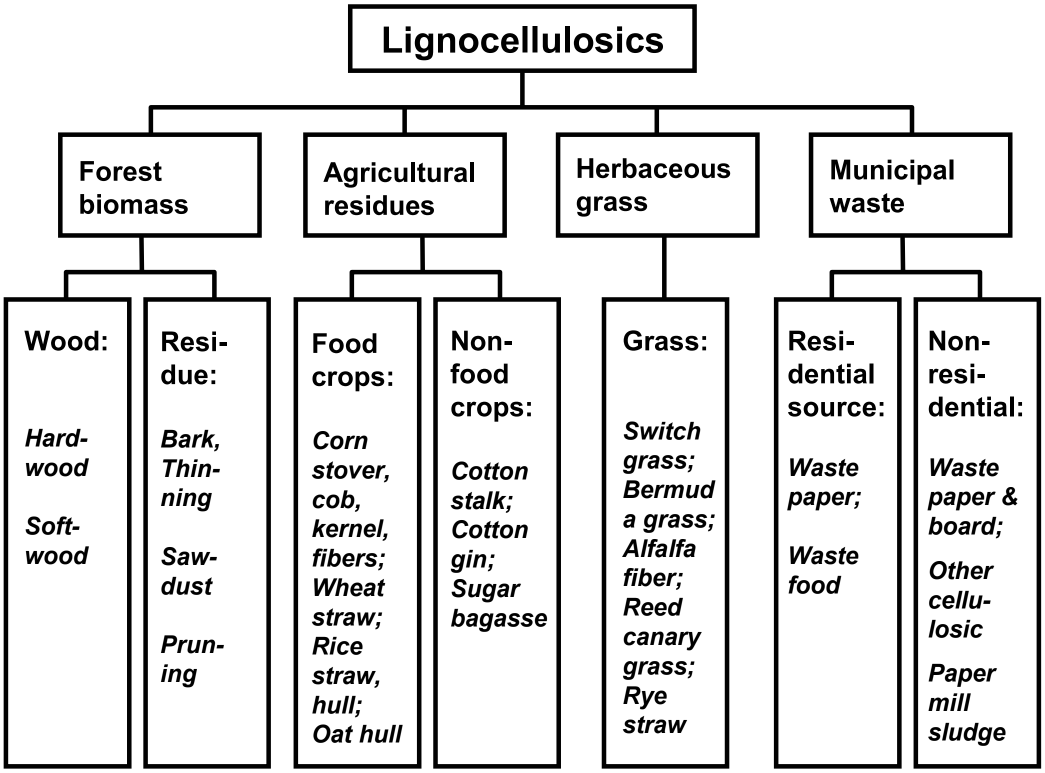

Fig. 1. Major lignocellulosics that have been explored for bioethanol production

Chemical Composition and Role of Pretreatment

Woody materials, including wood, bark, and mixtures of forest residues are composed of cellulose, hemicelluloses, lignin, and small amounts of other species (Fig. 2). Cellulose is composed of anhydro-glucopyranose, or glucose residue, which can be converted to glucose and provides the major source for hexose in woody biomass (Fig. 3). Cellulose is believed to have a highly crystallized structure due to the existence of hydrogen bonds. In contrast to its amorphous region, the crystalline region of cellulose make it hard to hydrolyze (Fig. 4). Hemicellulose is composed of both six-carbon sugars and five-carbon sugars, which include glucose, mannose, arabinose, xylose, and other species (Fig. 5). Xylose is believed to be present in the largest amount in hemicellolse**.** Unlike cellulose, hemicellose has a random and amorphous structure, which makes it easily be hydrolyzed by dilute acid or base. Lignin is the third major component in wood and comprises the glue that protects woody biomass from foreign invasion. It is mainly composed of phenolic units and represents the part of biopolymer that cannot be converted into ethanol directly or indirectly using the current technology. With the exclusion of lignin, the optimistic situation is to preserve and utilize all the carbohydrates and convert them into ethanol fuels. Pretreatments constitute the means to separate carbohydrates and lignin and disrupt the crystalline region of these materials; it should also downgrade carbohydrates as little as possible. Different pretreatment methods have been explored in order to achieve the optimistic situation.

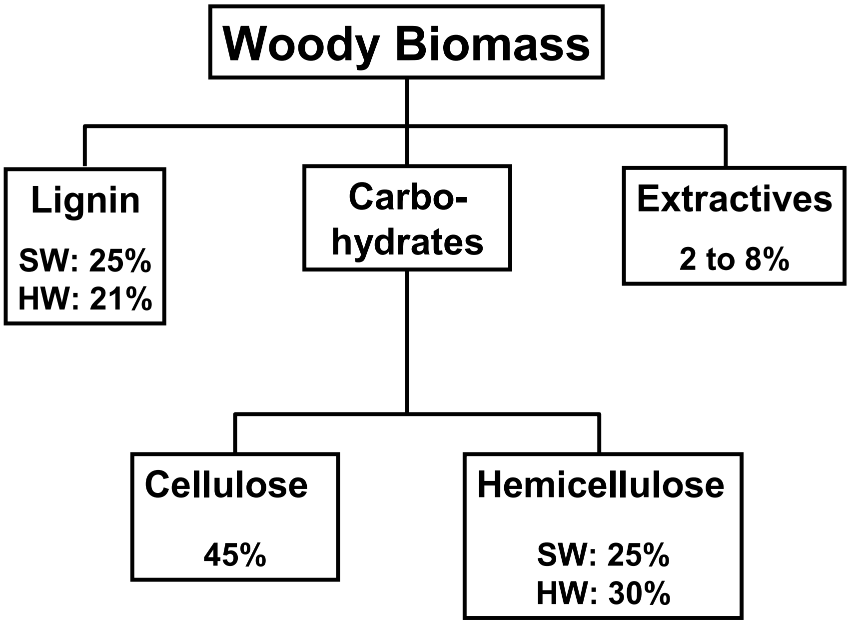

Fig. 2. Chemical composition of woody biomass

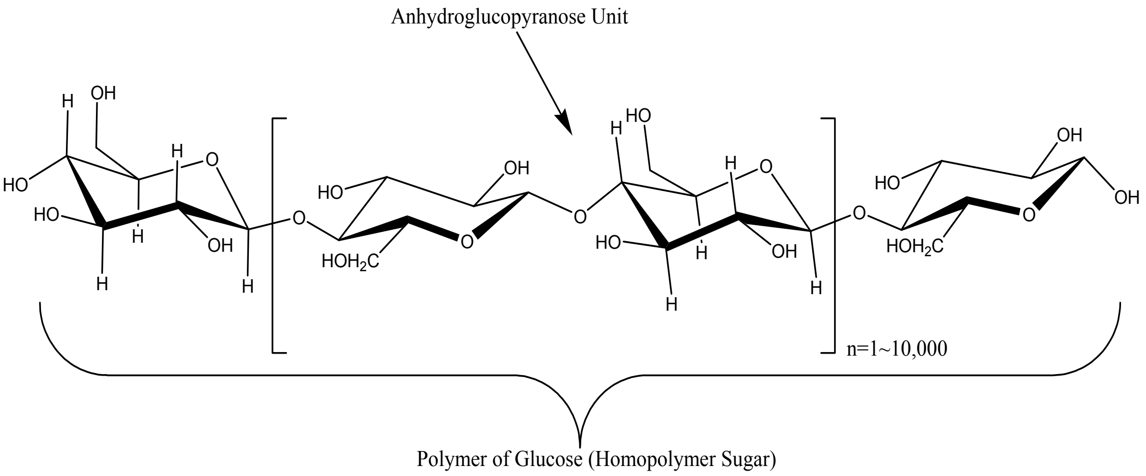

Fig. 3. Chemical structure of cellulose

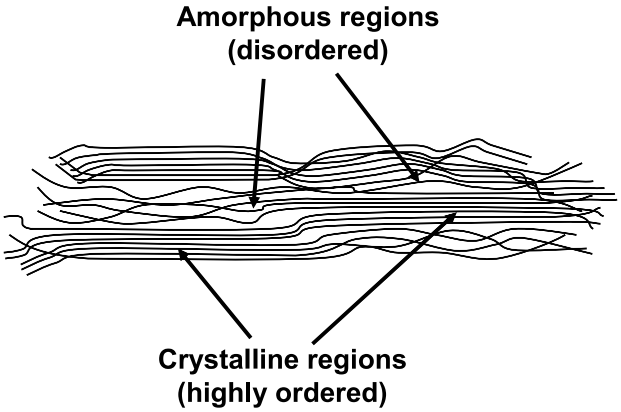

Fig. 4. Schematic drawing of cellulose microfibril

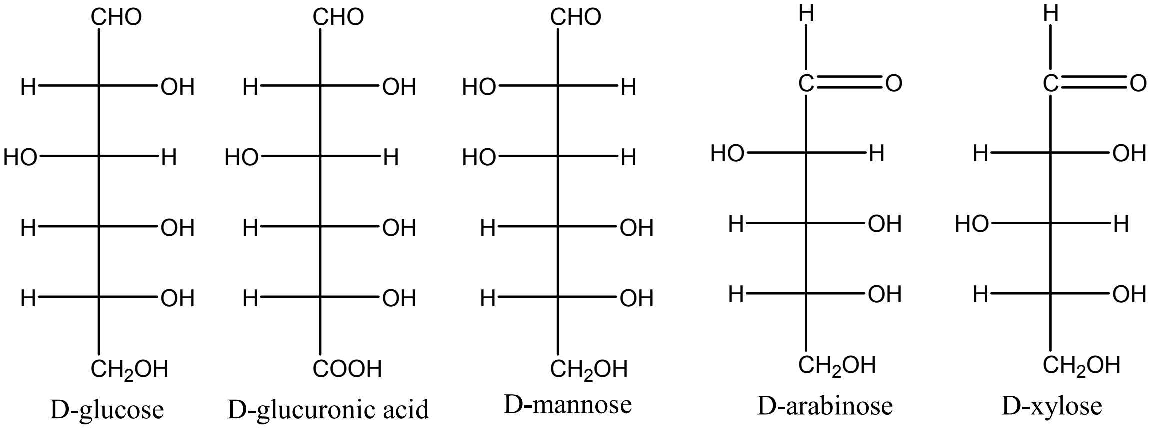

Fig. 5. Chemical compositions of hemicelluloses

In principle, the sugar chains can be hydrolyzed to monomeric sugars, most of which can be fermented to alcohol using yeast. Research is being done to improve the efficiency of transforming these sugars to ethanol. Two recent review articles have summarized in detail acid-based hydrolysis processes and enzyme based hydrolysis processes for ethanol from lignocellulosic materials (Taherzadeh and Karimi 2007a,b). The general approaches for the conversion of biomass to ethanol include the hydrolysis of the hemicellulose and the cellulose to monomer sugars, fermentation of these sugars, and product recovery and concentration by distillation. Figure 6 summarizes these steps.

The main difference between process alternatives in Fig. 6 is the hydrolysis, which can be acid hydrolysis, either dilute or concentrated, or enzymatic hydrolysis (Galbe and Zacchi 2002). Enzymatic hydrolysis has been thought to have the potential for higher yields and reduced formation of toxic compounds so that biomass ethanol is competitive when compared to other liquid fuels on a large scale (Wyman 1999). However, the enzymatic conversion of cellulose to sugar is extremely slow based on current technology. Part of the reason is that the cellulose is well protected by hemicellulose and lignin. It therefore entails pretreatment processes that expose cellulose in such materials or modify the pore structures so that enzymes can penetrate into fibers and hydrolyze cellulose more readily. After pretreatment, the hydrolysis of the carbohydrate fraction to monomeric sugars can be achieved faster and with greater yields.

PRETREATMENT CATEGORIES

In general, pretreatment can be classified into biological pretreatment, physical pretreatment, and chemical pretreatment according to the different force or energy consumed in the pretreatment process. Some pretreatment combines any two or all of these pretreatment and can produce subcategories. Table 2 summarizes some of the broadly explored pretreatment methods according to this classification (Sun and Cheng 2002b; Taherzadeh and Karimi 2007b).

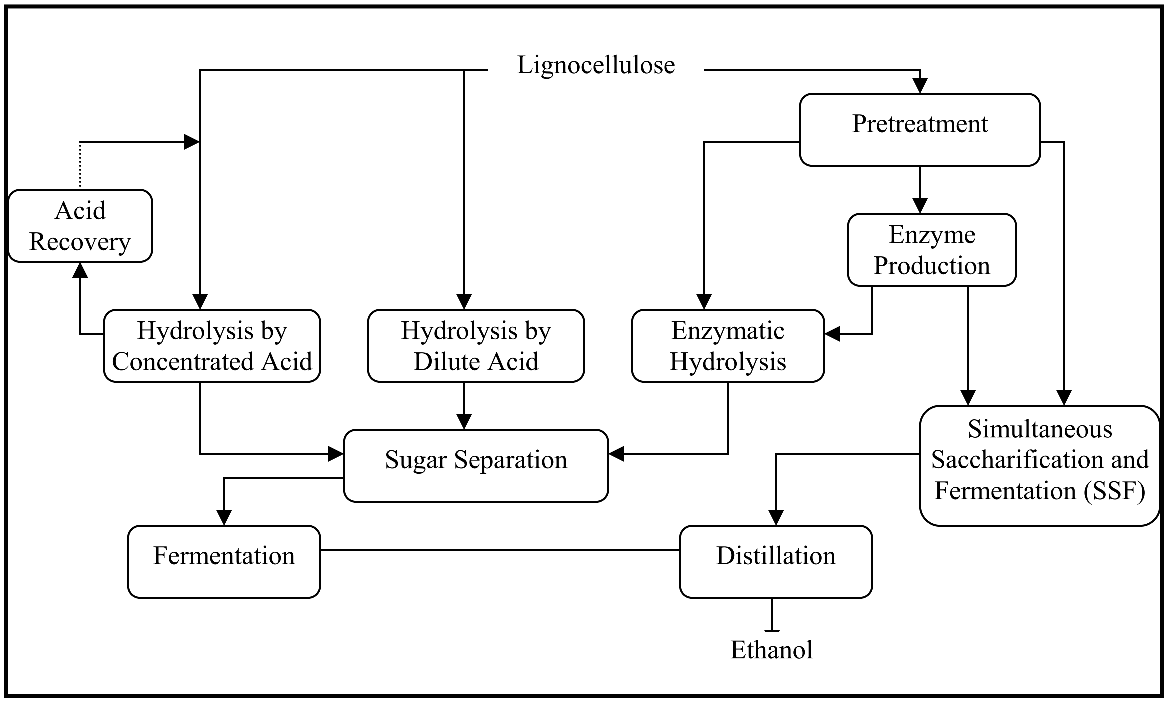

Fig. 6. Production of ethanol from lignocellulosic materials (Galbe et al. 2002)

Some methods that incorporate the combination of or more unit processes (McMillan 1994) have not been included in Table 2. Biological pretreatment has not attracted much attention, probably because of kinetic and economic considerations, although there has been various research showing biological pretreatment can be an effective way to recover sugars from different species of biomass (Kurakake et al. 2007; Taniguchi et al. 2005; Zhang et al. 2007). Physical and chemical pretreatments have been the subject of intensive research. Steam and water are usually excluded from being considered as chemical agents for pretreatment, since no extra chemicals are added to the biomass. Physical pretreatments include comminution, in which the particle sizes of the biomass are reduced with mechanical forces, steam explosion, and hydrothermolysis.

Comminution, including dry, wet, and vibratory ball milling (Millett et al. 1979; Rivers and Emert 1987; Sidiras and Koukios 1989), and compression milling (Tassinari et al. 1980, 1982), is sometimes needed to make material handling easier for the subsequent processing steps (Mosier et al. 2005). Electron beam pretreatment of used newsprint, pulp as well as pulp recovered from clarifier sludge and paper mill sludge has been explored for exploiting the cellulosic substance to make ethanol (Khan et al. 1986, 1987). It has also been used to pretreat softwood to enhance it enzymatic hydrolysis (Khan et al. 1986). Gamma-ray and microwave attracted some interest as well; research has shown their effects on the pretreatment of agricultural waste and other cellulosics-containing waste (Kim et al. 2007; Magara et al. 1989). In terms of the practicality and commercialization of physical pretreatment, steam pretreatment and hot water pretreatment have broader prospects. Publications have shown that these pretreatment methods have been attracting much more effort (Brandes and Graff 1985; Broglin 1996; Chandra et al. 2007; Galbe and Zacchi 2007; Saddler et al. 1993; Singh et al. 2004). Their effect on pretreated wood will be summarized later.

Acids or bases promote hydrolysis and improve sugar recovery yields from cellulose by removing hemicellulose or lignin during pretreatment. Sulfuric acid and sodium hydroxide are the most commonly used acid and base, respectively (Mosier et al. 2005). Another approach for pretreatment is to use liquid formulations capable of acting as solvents for cellulose. Work with cellulose solvent systems has shown that enzymatic hydrolysis could be greatly improved, but the work mainly has been restricted to agricultural residues and herbaceous grass. Little has been reported about the use of cellulose solvents in pretreating forest biomass such as wood, bark, or mixtures of such residues. A broad range of chemical pretreatments, such as alkaline peroxide, ozone, and organosolv, which uses Lewis acids such as $FeCl_3$, alum etc. in aqueous alcohols, as well as glycerol, dioxane, phenol, or ethylene glycol, have been suggested to disrupt the cellulose structure and promote its hydrolysis. Concentrated mineral acids (H_2SO_4, HCl), ammonia-based solvents (NH_3, hydrazine), aprotic solvents such as DMSO, metal complexes (ferric sodium tartrate, codexen, and cuoxan), as well as wet oxidation also reduce cellulose crystallinity, disrupt the association of lignin with cellulose, and dissolve cellulose. However, the economics of these methods do not permit any practical application when compared to the value of glucose (Mosier et al. 2005). Lime pretreatment and ammonia pretreatment have seemed to be the most attractive alkaline pretreatment, while most attention in acid pretreatment has been concentrated on the use of sulfur dioxide and sulfuric acid. These two acid pretreatments have also been combined to the steam pretreatment.

Research on the development of pretreatment technology applicable to ethanol production from woody biomass represents somewhat a different direction. The broadly explored pretreatment methods used in wood are summarized in Table 3. Table 3 lists the pretreatment methods and the mechanistic effect occurred as well. These methods, including steam explosion, liquid hot water, dilute acid, lime and ammonia pretreatment, are considered potentially cost-effective and could be used on a large scale in the future (Mosier et al. 2005). A deeper review of these methods follows, and the authors also propose acetic acid be used as catalyst for further alternatives for combining application of steam explosion pretreatment.

Table 2. Pretreatment Methods of Lignocellulosics for Enzymatic Hydrolysis

Pretreatment	Energy		Effect
	Source	Means	
Biological Pretreatment	Microbe	Fungi	Reduce DP of cellulose and hemicellulose
		Actinomycetes	Remove Lignin
Physical Pretreatment	Comminution	Ball Milling	Decrease particle size, cellulose crystallinity & DP Increase surface area and pore sizes Soften and partially deploymerize lignin Partialy hydrolyze hemicellulose
		Colloid Milling	
		Hammer Milling	
		Compression Milling	
	Irradiation	Electron Beam	
		Gamma-ray	
		Microwave	
	Hydrothermolysis	Liquid Hot Water	
	Steam Explosion	High Pressure Steam	
	Other Mechanical Energy	Expansion	
		Extrusion	
Chemical Pretreatment	Acid	carbonic acid	Decrease Crystallinity of Cellulose and its DP Partial or complete hydrolysis of hemicellulose Delignification
		hydrocholric acid	
		hydrofluoric acid	
		nitric acid	
		peracetic acid	
		phosphoric acid	
		sulfur dioxide	
		sulfuric acid	
	Alkaline	lime	
		sodium hydroxide	
		sodium carbonate	
		ammonia	
		ammonium sulfite	
	Gas	Chlorine dioxide	
		Nitrogen Dioxide	
	Oxidant	Hydrogen Peroxide	
		Ozone	
		Wet Oxidation	
	Cellulose Solvent	Cadoxen	
		CMCS	
		DMSO	
	Extraction of Lignin	Hydrozine	
		Ethanol-Water	
		Benzene-Water	
		Ethylen Glycol	
		Butanol-Water	
		Swelling Agent	

Table 3. Effect of Pretreatments on the Chemical Composition and Chemical/Physical Structure of Lignocellulosic Biomass (Mosier et al. 2005)

Pretreament Method	Accessible surface area increases	Cellulose Decrystalization	Hemicellulose Removal	Lignin Removal	Lignin Structure Alteration
Uncatalyzed steam explosion	●		●		○
Liquid hot water	●	ND	●		○
pH controlled hot water	●	ND	●		ND
Flow-through liquid hot water	●	ND	●	○	○
Dilute acid	●		●		●
Flow-through acid	●		●	○	●
Lime	●	ND	○	●	●
Ammonia freeze explosion(AFEX)	●	●	○	●	●
Ammonia recycled percolation(ARP)	●	●	○	●	●

●: Major Effect
○: Minor Effect
ND: Not Determined

Uncatalyzed Steam Explosion

Uncatalyzed steam explosion has been applied commercially to hydrolyze hemicellulose in the Masonite process, in which high-pressure steam is applied on wood chips in a large vessel without chemicals for several minutes, and then some steam is rapidly vented to reduce the pressure while the biomass is discharged into a large vessel for flash cooling. In this process, steam is used to promote hydrolysis of hemicellulose, and the process is terminated by explosive decompression (Avellar and Glasser 1998; Brownell and Saddler 1984; Glasser and Wright 1998; Heitz et al. 1991; Ramos et al. 1993). It is believed that the acetic acids and other acids released in the pretreatment hydrolyze the hemicellulose. Water itself may also act as an acid at high temperature. The expansion at the end of pretreatment terminates the reaction and opens up the particulate structure of wood. The removal of hemicellulose improves the accessibility of cellulose fibrils to enzymes, while the reduction in particle size and increased pore volume in this process is less important in improving the digestibility of the pretreated biomass.

Hot Water Pretreatment

Liquid hot water pretreatment uses pressure to keep water in a liquid state at elevated temperatures. Flow-through processes pass the liquid water at elevated temperatures through the cellulosic material. This method has been termed hydrothermolysis (Bobleter et al. 1981), aqueous or steam/aqueous fractionation (Bouchard et al. 1991), uncatalyzed solvolysis (Mok and Antal 1992), and aquasolv (Allen et al. 1996). This pretreatment usually has involved temperatures of 200-230 ºC for up to 15 minutes. Around 40-60% of the total mass is dissolved with 4-22% of the cellulose, 35-60% of the lignin, and all of the hemicellulose being removed (Mok and Antal 1992). It was found that temperature and time had little effect on the pretreatment results, while variability in results was attributed to different biomass types. Co-current, countercurrent, and flow-through are the major three types of liquid reactor configurations. The generation of acetic acids and other organic acids by cleaving O-acetyl and uronic acid substitutions from hemicellulose can both help and impede hot water pretreatment. The released acids help to catalyze formation and removal of oligosaccharides. On the other hand, released monomeric sugars could be further degraded to aldehydes if acid is used. These aldehydes, principally furfural from pentose and 5-hydroxymethyl furfural from hexose, are inhibitors to enzymes in fermentation (Palmqvist and Hahn-Hågerdal 2000a). The pH of pure water at 200 ºC is about 5.0. Water has an unusually high dielectric constant that enables ionic substances to dissociate. All hemicellulose can be dissolved by water; one half to two-thirds of the lignin also dissolves from most biomass when it is treated at 220 ºC for 2 min (Antal et al. 1996). Hemiacetal linkages are cleaved, and the released acids subsequently facilitate the breakage of such ether linkages. However, softwoods are less vulnerable to solubilization for reasons that are not well understood. There appears to have been no work showing successful pretreatment of softwood by hot water.

Acid Pretreatment

Work aimed at obtaining lignin from wood has proven that dilute acids are a good choice to disrupt the complex between lignin and carbohydrate (Guerra et al. 2006a,b; Wu and Argyropoulos 2003). Dilute acid pretreatment with sulfuric acid has been extensively researched because it is inexpensive and effective (Nguyen et al. 2000; Tengborg et al., 1998; Torget et al. 1990, 1991), although other acids such as nitric acid, hydrochloric acid and phosphoric acid have also been tested (Brink et al. 1999; Goldstein 1983; Goldstein and Easter 1992; Israilides et al. 1978). Dilute sulfuric acid is mixed with biomass to hydrolyze hemicellulose to xylose and other sugars, and then it can continue breaking xylose down to furfural (Fig. 7). The volatile fraction contains furfural, which can be recovered by distillation. The temperature for this pretreatment is usually at 150-220 ºC for seconds to minutes.

It is believed that acid hydrolysis releases oligomers and monosaccharides. It has been modeled as a homogeneous reaction in which the acid catalyzes breakdown of cellulose to glucose, followed by the breakdown of glucose to form 5-hydroxylmethyl-furfural and other degradation products. Different kinetic models have been adopted to describe the hydrolysis of hemicellulose and formation of furfural and other decomposition products (Converse et al. 1989; Esteghlalian et al. 1997; Kwarteng 1983; Lee et al. 1999). Carbohydrates are easily degraded to furfural and 5-hydroxymethylfurfural in acidic environments (Fig. 7). The further decomposition of these furan derivatives will result in the production of organic acids such as levulinic acid, formic acid, etc. (Fig. 7). These acids, as well as the furan derivatives, are inhibitors to the yeast used in the fermentation process. Meanwhile, the use of acid also imposes concerns related to the corrosion of equipment. The cost involved in pretreatment using only acid also hampers any practicality-oriented research and possible commercial application compared to the other pretreatments such as steam explosion or ammonia fiber explosion, which will be discussed hereafter.

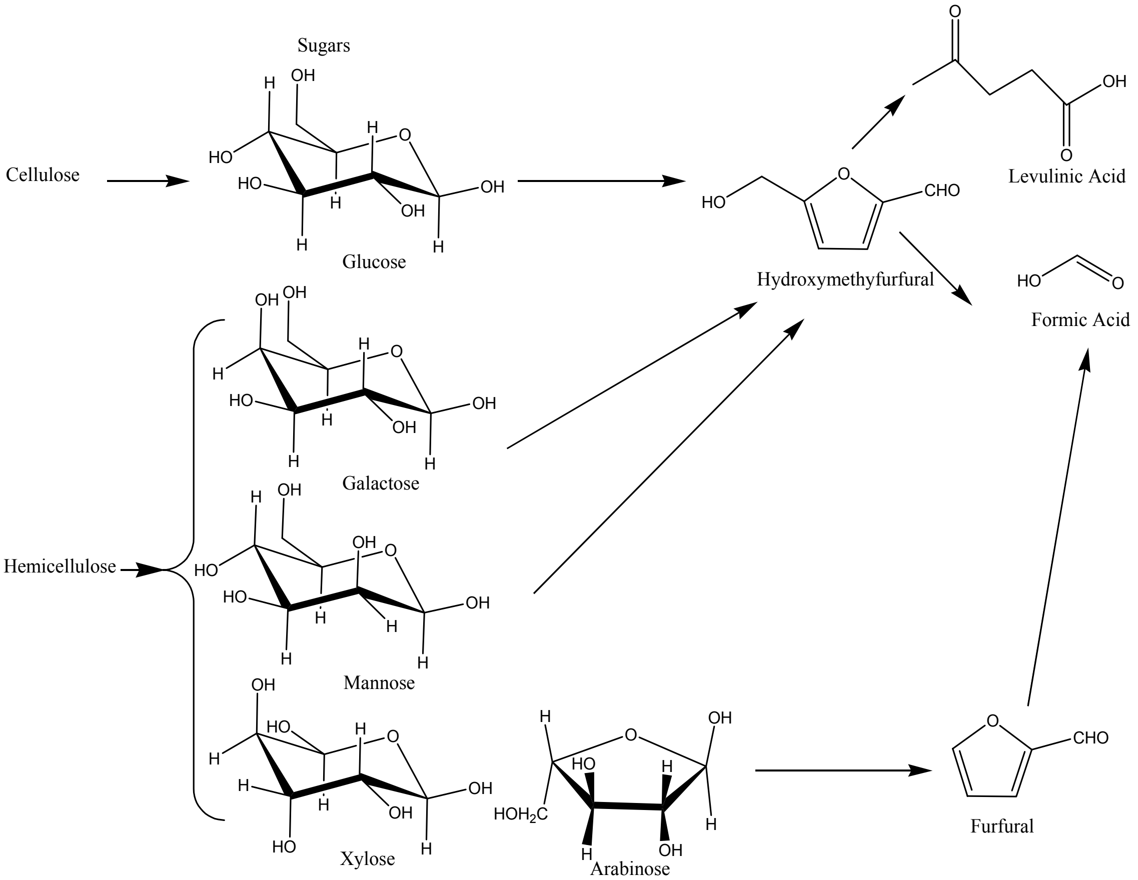

Fig. 7. Reactions occurring to carbohydrates during hydrolysis of lignocellulosic materials. The furan derivatives will react further to form levulinic acid and formic acid.

Steam Pretreatment with Acid Catalyst

Steam explosion using an acid catalyst has been under extensive investigation in recent years. It has been considered to be one of the most promising techniques for commercialization. Ongoing research is still aimed at optimization of its conditions or using different catalysts to fully exploit its advantages, as well as to improve the yield of overall sugars. Steam pretreatment with a sulfuric acid catalyst has been believed to be one of the most likely approaches that could be used commercially in the future. This combines the effect of both acids and steam. Pretreatment with SO_2 has also been thoroughly studied in combination with steam. However, SO_2 is probably less attractive, because of its high toxicity, which may pose safety and health risks. Its advantages lie in its lower corrosiveness and faster and easier penetration during the pretreatment process. The highest yield that has been achieved was about 82%, which was obtained through a two-stage pretreatment, in which the first one used comparatively low temperature, while the second one used a higher temperature. Among all of the one-stage steam pretreatment processes, the highest yield came with a lower dosage of sulfuric acid, which may testify to the hydrolytic effect of acid on carbohydrates (Galbe and Zacchi 2002). Table 4 summarizes some of the pretreatment conditions for acid-catalyzed steam pretreatment of softwood.

Since yield has been one of the important factors that determine the success of commercial production of ethanol from lignocellulosic biomass, further exploration of yield increase of sugars is worthwhile as long as it does not cause any significant increase in pretreatment cost.

Table 4. Pretreatment Conditions for Acid-Catalyzed Steam-Pretreated Softwoods (Galbe et al. 2005)

Substrate	Pretreatment Conditions			Yield[*](%)
	Catalyst	Temperature	Time	
Pine	4.44% SO_2	200 ºC	10 min	—
Spruce + Pine	2.0-2.6% SO_2	180-204 ºC	2min	—
Pine	0.5-12% SO_2	182-248 ºC	0.5-18min	—
Pine	2.0-2.6% SO_2	150-208 ºC	2-20min	—
Spruce	0.5-5% H_2SO_4	190-220 ºC	50-250s	—
Spruce	0.35% H_2SO_4	215 ºC	140s	—
Fir + Pine	0.4% H_2SO_4	200-230 ºC	125-305s	—
Spruce + Pine	1-6% SO_2	190-230 ºC	2-15min	66
Spruce	0.5-4% H_2SO_4	180-240 ºC	1-20min	67
Fir + Pine[a]	0.6-2.4% H_2SO_4	180-215 ºC	100-240s	75~82
	2.5% H_2SO_4	210 ºC	100-120s	
Spruce[a]	0.5% H_2SO_4	180 ºC	10min	77~80
	1-2% H_2SO_4	180-220 ºC	2-10min	

[a] Two-stage pretreatment

[*] yield of sugar as of percent of the theoretical in raw material

Alkaline Pretreatment

Alkaline pretreatment uses low temperature and pressure. It even may be carried out under atmospheric conditions, but the pretreatment time could be hours or even days rather than seconds or minutes. In lime pretreatment, some calcium is converted to irrecoverable salts or incorporated into the biomass. This pretreatment method has also been evaluated with addition of oxygen or air. Chang et al. (2001) used this method to treat poplar wood at 150 ºC for 6h with 14-atm oxygen. Other alkali pretreatment formulations include sodium, potassium, calcium, and ammonium hydroxide as reactants. Sodium hydroxide receives the most attention, but lime has the advantage of being a low cost and safe agent, as well as being easily recoverable from water as insoluble $CaCO_3$ by reaction with CO_2. Then the $CaCO_3$ can be converted to lime, using lime kiln technology. Addition of air/oxygen improves the delignification of biomass.

Alkaline pretreatment is similar to Kraft pulping, in which lignin is removed, thus improving the reactivity of the remaining polysaccharides. Meanwhile, acetyl groups and the various uronic substitutions on hemicellulose are also removed so that there is less hindrance for enzymes to access the surface of hemicellulose and cellulose.

Ammonia Pretreatment

Ammonia treatment is also, in a strict sense, alkaline treatment. However, it is often considered separately due to its effectiveness and potential benefits in treating agricultural residues and herbaceous materials. Ammonia fiber/freeze explosion (AFEX) pretreatment has been the most frequently evaluated pretreatment of all alkaline pretreatments. Ammonia fiber/freeze pretreatment uses anhydrous liquid ammonia to treat cellulosic materials in a pressure vessel in the weight ratio of about one to one at ambient or room temperature, and under the vapor pressure of liquid ammonia at said ambient temperature. The mixture is stirred for a certain period of time sufficient for the ammonia to wet and swell the cellulose or cellulose-containing material. At the end of this treatment, the pressure is rapidly reduced to atmospheric, which allows the ammonia to boil. Contact of the material with the ammonia is maintained at the boiling point of the ammonia, which essentially freezes the cellulose-containing material. When treatment is completed, the treated material is separated from the liquid and gaseous ammonia, which is recovered for recycling (Dale 1986). The ammonia freeze explosion pretreatment simultaneously reduces lignin content and removes some hemicellulose, while decrystallizing cellulose. Thus it affects both micro- and macro-accessibility of cellulases to cellulose (Mosier et al. 2005). Liquid ammonia pretreatment may cause mercerization, which spurs cellulose swelling and a phase change from cellulose I to cellulose II. Ammonolysis of glucuronic cross-links makes the carbohydrate more accessible by cellulases (Schwertassek and Hochman 1974).

Pretreatment with aqueous ammonia in a flow-through mode involves putting 5-15% ammonia solution through a column reactor that has been packed with the biomass. Operating conditions of 160-180 ºC and 14 min of residence time can be used (Iyer et al. 1996; Yoon et al. 1995). Under these conditions, aqueous ammonia cleaves lignin-carbohydrate linkages and depolymerizes lignin. Due to the reaction between ammonia and water, the resultant species include the hydroxyl ion, whose existence makes this process somewhat similar to an alkaline pulping process. Pretreatment with aqueous ammonia is also known as the ammonia recycled percolation process (ARP). Although it has been reported that a large and adjustable degree of delignification results from tests with hardwood (Yoon et al. 1995)and agricultural residues (Iyer et al. 1996) at 160-180 ºC for 14min, it was less efficient in pretreating softwood-based pulp mill sludge (Kim et al. 2000).

AFEX pretreatment yields optimal hydrolysis rates for pretreated lignocellulosics, with close to theoretical yields at low enzyme loadings. It has some unique features that distinguish it from other biomass treatments (Teymouri et al. 2005):

- Nearly all of the ammonia can be recovered and reused, while the remaining portion serves as a nitrogen source for microbes, in downstream processes.
- There is no wash stream in the process. Dry matter recovery following the AFEX treatment is essentially 100%. AFEX is basically a dry-to-dry process. Treated biomass is stable for long periods and can be fed at very high solids loadings in enzymatic hydrolysis or fermentation processes.
- Cellulose and hemicellulose are well preserved in the AFEX process, with little or no degradation. There is no need for neutralization prior to the enzymatic hydrolysis of AFEX-treated biomass.
- Enzymatic hydrolysis of AFEX-treated biomass produces clean sugar streams for subsequent fermentation process.

AFEX is well suited for agricultural and herbaceous residues, but it works only moderately well on hardwoods and is not well suited for softwoods (Mosier et al. 2005). Possible reasons for this could be directly related to the anatomical properties of different cells, since softwood fibers' lumens are thinner and its cell walls are thicker, which might make the mass transport of ammonia much slower. From a chemical viewpoint, the lignin-carbohydrate complex might be harder to disrupt, while the higher lignin content could make lignin itself harder to degrade. The mass transport of degraded species might be much slower due to the combination of these effects.

The cost of ammonia and especially of ammonia recovery determines the cost of this pretreatment (Holtzapple 1992). Nevertheless, total sugar yield affects the overall economics more strongly. This depends on the loss in yield as well as sugar degradation, which could produce inhibitory products impacting the downstream fermentation. Fortunately, the moderate temperatures (<90 ºC) and pH values (<12.0) of the AFEX treatment minimize formation of sugar degradation products, while giving high yields. AFEX is among the more promising pretreatment methods for application with lignocellulosic biomass of lower lignin content.

PERSPECTIVES FOR FUTURE RESEARCH ON WOOD BARK AND FOREST RESIDUES

Currently available pretreatment techniques have provided a broad range of choices that improve the conversion of carbohydrates from lignocellulosic biomass to ethanol. In general, these techniques focus on disrupting the protection of cellulose and hemicellulose by lignin, as well as dissociation between cellulose and hemicellulose. Some of these changes occurring to biomass also decrease the crystallinity of cellulose and increase the specific surface area that cellulase enzymes can access. For softwood and bark biomass, the use of steam explosion with an acidic catalyst seems more promising compared to the current technologies due to their high lignin contents. For some wood bark or sawdust biomasses, if they have less lignin content as well as low densities, AFEX could be an alternative that takes advantage of moderate temperature pretreatment. Increase of the treatment time of AFEX might also work effectively in the case of biomass with comparatively high lignin content such as softwood.

Although steam pretreatment with sulfuric acid or sulfur dioxide as a catalyst has been broadly explored and proved to be effective in treatment of softwood, the presence of sulfur could impose potential threats to some enzymes. It could also cause problems in downstream purification and distillation of products. Furthermore, increased content of sulfur in the final product may incur environmental problems, such as increased emission of SO_2 when ethanol produced is used in vehicles once residual sulfur is carried over to the final product. Unfortunately, no work has been performed to evaluate such effects. The authors believe that the evaluation of this effect will be carried out some day when more ethanol is being made by using these techniques. Considering the autocatalysis effect concomitant with the production of acetic acid or uronic acid from pretreatment of hardwood, we think that using acetic acid as a catalyst could be a better choice than either sulfuric acid or SO_2. Meanwhile, we expect that acetic acid should not have any obviously detrimental effect on cellulase enzymes, since most of those enzymes show their optimal enzymatic activity within the pH range of 4.5~5.5. In addition, this would probably not cause extra problems of inhibition to fermentation or contamination of the final product. With appropriate control of the dosage of acetic acid, there should not be any inhibitory effect on either cellulase or yeast (Taherzadeh et al. 1997). There is potential to develop acid pretreatment using acetic acid as an alternative.

Ammonia fiber explosion (AFEX) is another promising pretreatment that has been thought to have potential benefits that are both economical and environmental. Current research shows it works well on agricultural residues and hardwood but not on softwood. It has not been evaluated on bark and sawdust. It may be possible to modify AFEX, which uses anhydrous liquid ammonia to pretreat biomass, to treat softwood by extending the pretreatment time. Further research should be conducted to facilitate its use on softwoods.

Generally speaking, we think that the criteria set by the National Research Council provide some general rules to aid in exploration of any pretreatment methods (National Research Council 1999):

1. Avoid the need for reducing the size of biomass particles so that less mechanical energy will be consumed.
2. Preserve the pentose (hemicellulose) fractions to completely use the carbohydrates.
3. Limit the formation of degradation products that inhibit growth of fermentative microorganisms in order to improve the efficiency of enzyme and microbe.
4. Minimize energy demands.
5. Limit overall costs.

These criteria, as well as the generation of a higher-value lignin co-product, form a basis of comparison for various pretreatment options.

Evaluation of Pretreatment Effect

A number of screening variables can be used to evaluate pretreatment effects. These variables can be water retention value (WRV), porosity of pretreated biomass, crystallinity of cellulose, specific surface area of pretreated biomass, and degree of polymerization. However, the complexity of the saccharification and fermentation processes makes it difficult to check the overall performance of the pretreatment and evaluate the potential of pretreatment materials to ethanol using any of these simple screening variables**.** Sugar yield is one of the most direct indexes to determine pretreatment effect as far as the conservation of carbohydrates is concerned. Enzymatic hydrolysis of the pretreated biomass would be the appropriate way to check this. It is a good scientific approach to check their effects on cellulase and yeast to separate chemical species in pretreated biomass. This approach needs to involve separate hydrolysis and fermentation (SHF); it may also need to evaluate different species individually, as has been done by different researchers (Klinke et al. 2001; Palmqvist and Hahn-Hågerdal 2000a, 2000b). In a commercial setting, the biggest advantage for SHF is that both unit operations can be performed at their optimum operating conditions. However, the hydrolysis can be easily inhibited by either cellobiose or glucose, because both the endoglucanase or exoglucanase and β-glucosidase are end-product inhibiting enzymes. The other approach is the so-called simultaneous saccharification and fermentation (SSF). The produced sugar in SSF will be converted into ethanol, which is much less inhibitory to these isozymes. Meanwhile, SSF is a simpler approach from the viewpoints of capital cost and process consideration. SSF will therefore be a more promising strategy applicable to commercial environments. An experimental simulation of SSF in the laboratory will give a more productive evaluation than other screening process.

Figure 8 illustrates a general approach for ethanol production, which provides information on different stages that should be considered when one considers further exploration of this process. Review articles provide further information on SSF (Sun and Cheng 2002a; Taherzadeh and Karimi 2007b).

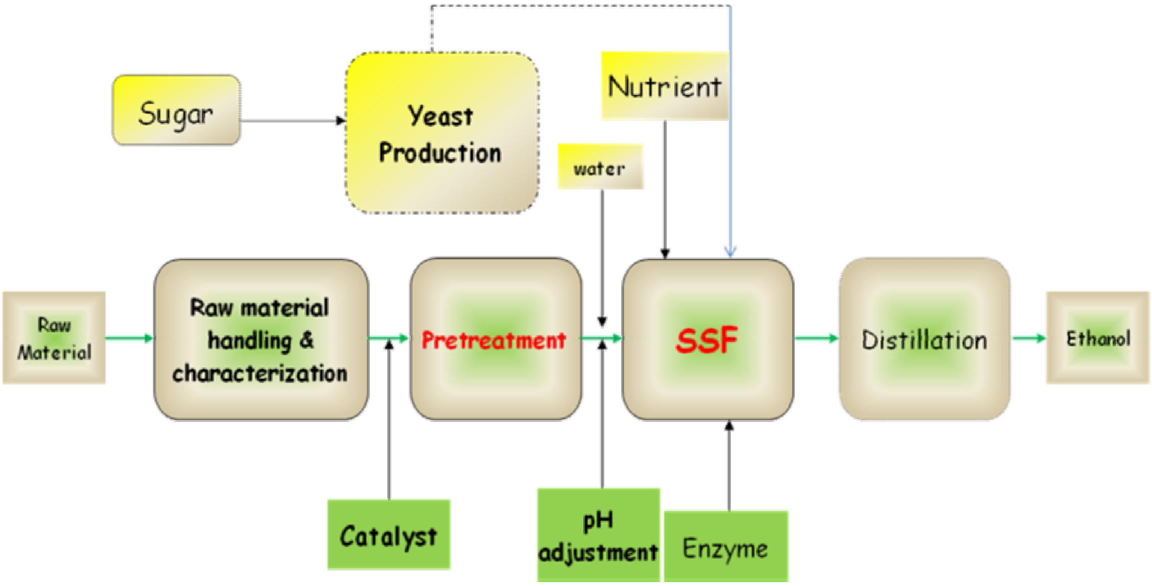

Fig. 8. Basic unit operations for ethanol biorefinery from forest residues

Economic Estimation of Cost Related to Chemicals and Energy in Pretreatment

Economic analysis is less meaningful in a laboratory scale than for a simulated real production situation. It is necessary to point out that assumptions are needed in order to achieve a comparatively credible estimate. In any practical situation, the overall capacity must be at a scale that is large enough to produce economical benefits. Two thousand metic tons per day of biomass would be a reasonable assumption. Two scenarios are considered for our approximation, without the consideration of capital cost, operational cost, etc. One is steam explosion with acetic acid as catalyst, and the other one is ammonia fiber explosion. Elaborations for these two are discussed subsequently, but chemical cost and energy cost are estimated. Capital and operating costs are not included in these estimates.

Pretreatment Cost for Steam Explosion with Acetic Acid as Catalyst

In the case of steam explosion with acetic acid as catalyst, the assumptions are as follows: Acetic acid impregnates the biomass under room temperature conditions. Considering the acid dissociation constant and effect of temperature, the threshold concentration can be set at about 1 mM for the liquid part, which corresponds to a pH value of about 3.9, and the treatment has a catalytic effect to dissociate the complex between carbohydrates and lignin. The pH value calculations are based on the dissociation constant of $K_a=1.8\times10^{-5}$. After impregnation, the biomass is brought into a steam cooker. The temperature is assumed to remain at 200°C for 10 minutes after heating up from normal temperature, which is assumed to be 25 °C on average. Heating up is assumed to take one minute. The solid concentration is taken as 25%. For the simplification of calculations, the major energy consumption of steam is assumed to be consumed during the heating up process, in which the temperature change is 175°C. In order for the hypothetical pretreatment to use steam from a pulp or paper mill's recovery boiler, the steam pressure is assumed to have a pressure of 175psig. The specific heat of wood after it is impregnated in dilute acetic acid is assumed to be the same as that of water, although this could be much lower in the case of oven-dry wood. The estimated energy and chemical cost for this scenario is around $18.88 per metric ton of dry mass. If the solid concentration is raised to 33%, then the estimated pretreatment cost will be about $15.28. The total pretreatment costs in both situations are less than 20 dollars; 95% of the cost will be spent on energy. It can also be seen that higher pretreatment solids content results in lower pretreatment costs. Table 5 summarizes the conditions for steam explosion pretreatment with acetic acid as catalyst, as well as the cost estimates.

Table 5: Hypothetic Conditions for Steam Explosion with Acetic Acid and its Cost Estimation

Pretreatment Conditions					
Acetic acid concentration	pH	Solid concentration	Heat-up time	Pretreatment Time	Pretreatment Temperature
1 mM	3.9	25% (33%)	1 min	9 min	200°C
Cost Estimation					
Chemical		Steam			
[1]Acetic Price	Cost ($/OD on)	Price	Pressure (psi)	[2]Latent Heat	Cost ($/OD Ton)
1.35~1.41$/kg	0.24	[3]$6 /1000 lb ($.0132/kg)	175	2000 kJ/kg	15.04 (18.64)
Total Pretreatment Cost ($/ OD ton biomass)			18.88 (15.28)		

[1] Information from Chemical Economics Handbook(Anonymous)
[2] (Anonymous)
[3] Personal communication with Dr. Hasan Jameel, NCSU
[4] Specific heat of water: 4.186 kJ/kg

Cost Estimation for Ammonia Fiber Explosion

Estimating the cost for ammonia fiber explosion is different due to the recycling of ammonia if capital cost estimation is involved. But if we only consider the energy and chemical cost, the calculation won't be substantially different for the previous case. In this scenario, the pretreatment is assumed to be carried out at 60% moisture content for biomass; the pretreatment temperature is maintained at 90 °C at a pressure of 250~300 psi for 5 minutes. As in the scenario for steam explosion with acetic acid as catalyst, steam of 175 psi is used to reach the desired temperature. The use of anhydrous liquid ammonia is assumed. A jacketed pretreatment reactor is assumed to be used, so that there is no mixing between steam and ammonia, which would help to reduce extra moisture addition. The recycling ratio of ammonia is assumed to be 99%.

Energy needed to heat up liquid ammonia can be estimated from the enthalpy change of ammonia at different states. The enthalpy of saturated liquid ammonia at 25 °C is 298.8 kJ/kg.K, while that of the superheated ammonia at 90°C is 1604.94 kJ/kg.K. The difference between these enthalpies is used to determine how much energy is used, as well as similar enthalpy differences for wood and moisture. A simple approach is sketched in Fig. 9 to estimate this energy demand for heating up liquid ammonia.

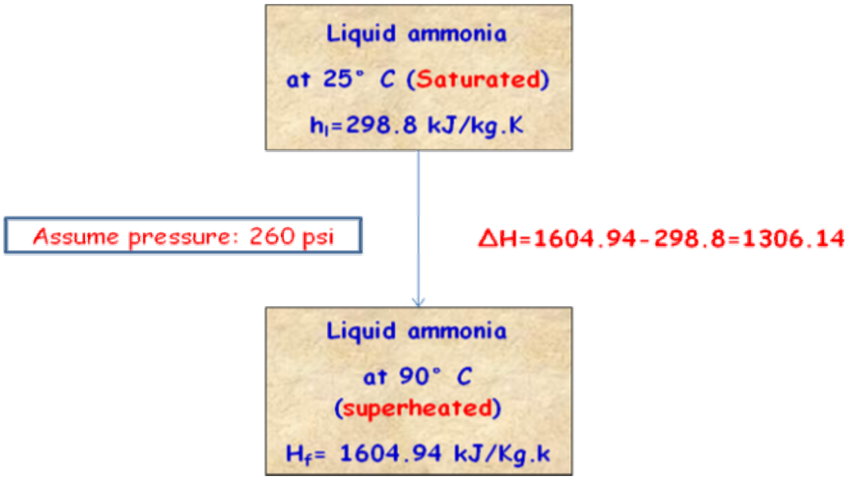

Fig. 9. Enthalpy changes for ammonia used in pretreatment

The energy needed to make this enthalpy change happen is ΔH = 1604.94 - 298.8 = 1306.14 kJ/kg.K, which should be included in the calculation of the corresponding steam consumption for pretreatment. With these assumptions the pretreatment cost should be about $12.28 per metric ton of dry biomass. Table 6 shows the costs for AFEX pretreatment as well as a summary of the corresponding pretreatment conditions. We can see that the total estimated pretreatment cost for AFEX is lower than steam pretreatment with acid catalyst, and so is the cost ratio for energy.

It is necessary to mention that no energy would be needed in the recovery of gaseous ammonia to 25°C after AFEX. Since the boiling point for liquid ammonia is -33.5°C, it has more enthalpy that could be extracted and used in other places in the manufacturing operation, which can make the process more cost-effective if the latent heat of ammonia were used when it is converted back to the liquid state for reuse. However, some extra capital cost would be needed for the installation of recovery equipment, such as a compressor or heat exchanger, as well as equipment for separation of residual water when needed, which is not in the scope of the discussion here. The energy consumption for a compressor is not included here, either.

It can be seen that AFEX is more cost-competitive based on the above cost estimation. Successful breakthrough in application of this method to forest residues can broaden the way through which bioethanol capacity can be increased greatly.

Table 6: Pretreatment Conditions for AFEX and its Cost Estimation

<table>
<tr><td colspan="6">Pretreatment Conditions</td></tr>
<tr><td>Ammonia Loading</td><td>Recycling ratio of Ammonia</td><td>Moisture content</td><td>Heat-up time</td><td>Pretreatment Time</td><td>Pretreatment Temperature</td></tr>
<tr><td>1 ton/ ton OD biomass</td><td>99%</td><td>60%</td><td>30s</td><td>5 min</td><td>90°C</td></tr>
<tr><td colspan="6">Cost Estimation</td></tr>
<tr><td colspan="2">Chemical</td><td colspan="4">Steam for pretreatment</td></tr>
<tr><td>[1]Anhydrous Liquid Ammonia</td><td>Cost ($/ OD Ton)</td><td>Price</td><td>Pressure (psi)</td><td>[2]latent heat</td><td>Cost ($/OD Ton)</td></tr>
<tr><td rowspan="2">0.18 $/kg</td><td rowspan="2">1.8</td><td>3$ /1000 lb (0.67¢/kg)</td><td>175</td><td>2000 kJ/kg</td><td rowspan="2">10.48</td></tr>
<tr><td>[4]Specific heat (C_p)</td><td colspan="2">1.465 kJ/Kg.K</td></tr>
<tr><td colspan="3">Pretreatment Cost ($/ OD ton biomass)</td><td colspan="3">12.28</td></tr>
</table>

[1] Information for Chemical Economics Handbook(Anonymous)
[2] http://www.chemicalogic.com/download/mollier.html(Anonymous)
[3] Specific heat of water: 4.186 kJ/kg
[4] Specific heat of dry wood is assumed to be 35% of water (McMillin, 1969)

CONCLUSION

Much research has been performed on utilization of biomass to make ethanol; most of this work has been focused on agricultural residues, especially corn stover. Less work has been carried out on using forest residues directly, especially on wood bark, although some work has been directed at wood itself. This paper briefly reviews different pretreatment methods that have been explored. Emphasis was placed on those attracting much interest for the pretreatment of woody biomass. The intention of this review is to shed some light on using whole wood, as well as forest residues, to produce ethanol. The authors are also trying to propose the use of acetic acid as catalyst to pretreat woody biomass.

A simple economic estimation for pretreatment of forest residue shows that AFEX is more promising in terms of operating costs. More important is that this method consumes less energy, while it also maintains a lower total pretreatment cost. However, it must be developed further for use on softwoods and more comprehensive analysis is needed based on experimental data in the future for its application. Estimation of costs involving capital and operation should also be included when it comes to commercial application. The authors hope that this review and the suggestions proposed can expand our insight in understanding pretreatment and provide a reference to facillitate commercialization of bioethanol derived from forest residues.

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Article submitted: Oct. 22, 2007; Peer-review completed: Jan. 14, 2008; Revised version received and accepted: Feb. 11, 2008; Published: Feb. 12, 2008; Erratum: Feb. 25, 2008, Fig. 5 was changed to show the label “D-glucuronic acid” instead of “glucose”.