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Features of promising technologies for pretreatment of lignocellulosic biomass

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Abstract

Cellulosic plant material represents an as-of-yet untapped source of fermentable sugars for significant industrial use. Many physio-chemical structural and compositional factors hinder the enzymatic digestibility of cellulose present in lignocellulosic biomass. The goal of any pretreatment technology is to alter or remove structural and compositional impediments to hydrolysis in order to improve the rate of enzyme hydrolysis and increase yields of fermentable sugars from cellulose or hemicellulose. These methods cause physical and/or chemical changes in the plant biomass in order to achieve this result. Experimental investigation of physical changes and chemical reactions that occur during pretreatment is required for the development of effective and mechanistic models that can be used for the rational design of pretreatment processes. Furthermore, pretreatment processing conditions must be tailored to the specific chemical and structural composition of the various, and variable, sources of lignocellulosic biomass. This paper reviews process parameters and their fundamental modes of action for promising pretreatment methods.
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1. Introduction

Environmental, long-term economic and national security concerns have motivated research over the last 25 years into renewable, domestic sources of fuels and chemicals now mostly derived from petroleum. Currently practiced technologies in US industry are based on the fermentation of glucose derived from corn starch. The US fuel ethanol industry represents an on-going success story for the production of renewable fuels. According to the Renewable Fuels Association (2003), the US annual fuel ethanol capacity was 2.9×10^9 US gallons in 2002, an increase of 10^9 US gallons over the production level in 2000. This industry forms an infrastructure from which future growth in cellulosic substrates utilization may occur. Demand for fuel ethanol is expected to increase. In addition to ethanol, forty chemicals and chemical feedstocks have been identified as potential products from renewable plant biomass (Ladisch et al., 1979; Voloch et al., 1985; Landucci et al., 1996; Ladisch, 2002).

Pretreatment is an important tool for practical cellulose conversion processes, and is the subject of this article. Pretreatment is required to alter the structure of

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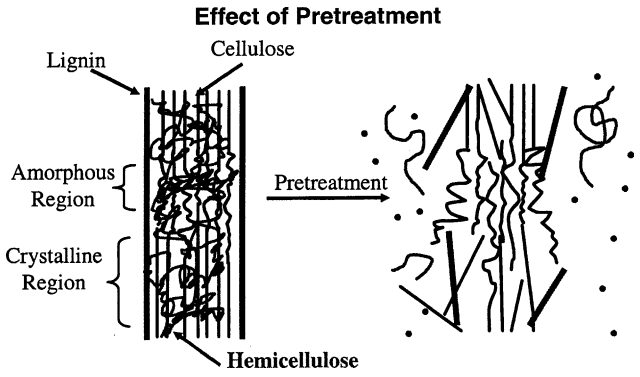

Fig. 1. Schematic of goals of pretreatment on lignocellulosic material (adapted from Hsu et al., 1980).

cellulosic biomass to make cellulose more accessible to the enzymes that convert the carbohydrate polymers into fermentable sugars as represented in the schematic diagram of Fig. 1. The goal is to break the lignin seal and disrupt the crystalline structure of cellulose. Pretreatment has been viewed as one of the most expensive processing steps in cellulosic biomass-to-fermentable sugars conversion with costs as high as 30¢/gallon ethanol produced. Pretreatment also has great potential for improvement of efficiency and lowering of cost through research and development (Lynd et al., 1996; Lee et al., 1994; Kohlman et al., 1995; Mosier et al., 2003a,b).

2. Ethanol process overview

Processing of lignocellulosics to ethanol consists of four major unit operations: pretreatment, hydrolysis, fermentation, and product separation/purification. Pretreatment is required to alter the biomass macroscopic and microscopic size and structure as well as its submicroscopic chemical composition and structure so that hydrolysis of the carbohydrate fraction to monomeric sugars can be achieved more rapidly and with greater yields. Hydrolysis includes the processing steps that convert the carbohydrate polymers into monomeric sugars. Although a variety of process configurations have been studied for conversion of cellulosic biomass into ethanol, enzymatic hydrolysis of cellulose provides opportunities to improve the technology so that biomass ethanol is competitive when compared to other liquid fuels on a large scale (Wyman, 1999).

Cellulose can be hydrolytically broken down into glucose either enzymatically by cellulases or chemically by sulfuric or other acids. Hemicellulases or acids hydrolyze the hemicellulose polymer to release its component sugars. Glucose, galactose, and mannose, six carbon sugars (hexoses), are readily fermented to ethanol by many naturally occurring organisms, but the pentoses xylose and arabinose (containing only five carbon atoms) are fermented to ethanol by few native strains,

Table 1
Percent dry weight composition of lignocellulosic feedstocks

Feedstock	Glucan (cellulose)	Xylan (hemicellulose)	Lignin
Corn stover[a]	37.5	22.4	17.6
Corn fiber[b,c]	14.28	16.8	8.4
Pine wood[d]	46.4	8.8	29.4
Popular[d]	49.9	17.4	18.1
Wheat straw[d]	38.2	21.2	23.4
Switch grass[d]	31.0	20.4	17.6
Office paper[d]	68.6	12.4	11.3

Note: Because minor components are not listed, these numbers do not sum to 100%.

[a] Data from Elander, R. Personal communication, National Renewable Energy Laboratory, Golden, CO, 2002.

[b] Also contains 23.7% by dry weight starch.

[c] Unpublished data from Laboratory of Renewable Resources Engineering, Purdue University.

[d] From Wiselogel et al. (1996).

and usually at relatively low yields. While pentoses are not readily fermented, the ketose of xylose, xylulose, is converted to ethanol by *S. pombe*, *S. cerevisiae*, *S. amucae,* and *Kluveromyces lactis* (Gong, 1983). Xylose and arabinose generally comprise a significant fraction of hardwoods, agricultural residues, and grasses (Table 1) and must be utilized to make the economics of biomass processing feasible (Lynd et al., 1999). Genetic modification of bacteria (Ingram et al., 1998, 1999) and yeast (Ho et al., 1998, 1999) has produced strains capable of co-fermenting both pentoses and hexoses to ethanol and other value-added products at high yields.

Enzymatic hydrolysis performed separately from the fermentation step is known as separate hydrolysis and fermentation (SHF). Cellulose hydrolysis carried out in the presence of the fermentative microorganism is referred to as simultaneous saccharification and fermentation (SSF). Simultaneous saccharification of both cellulose (to glucose) and hemicellulose (to xylose and arabinose) and co-fermentation of both glucose and xylose (SSCF) would be carried out by genetically engineered microbes that ferment xylose and glucose in the same broth as the enzymatic hydrolysis of cellulose and hemicellulose. SSF and SSCF are preferred since both unit operations can be done in the same tank, resulting in lower costs (Wright et al., 1988).

Ethanol is recovered from the fermentation broth by distillation or distillation combined with adsorption (Gulati et al., 1996; Ladisch and Dyck, 1979; Ladisch et al., 1984). The residual lignin, unreacted cellulose and hemicellulose, ash, enzyme, organisms, and other components end up in the bottom of the distillation column. These materials may be concentrated, and burned as fuel to power the process, or converted to various coproducts (Wyman, 1995a; Hinman et al., 1992; Wooley et al., 1999). The focus of this review is on the first processing step, pretreatment, and how this processing step affects downstream processing performance.

A study performed for the US Department of Energy (Reynolds, 2002) reported "no major infrastructure barriers exist" for producing and using over 5×10^9 US gallons of ethanol across the country each year. Cellulosic plant materials represent an as-of-yet untapped source of fermentable sugars for industrial use, and include corn stover, wood chips, and "energy crops" currently under development (Lynd et al., 1999).

3. Influence of biomass composition and structure on cellulose hydrolysis

Unless a very large excess of enzyme is used, the enzymatic digestibility of the cellulose in native biomass is low (<20% yield) because of its structural characteristics. Cellulosic biomass, sometimes called lignocellulosic biomass, is a heterogeneous complex of carbohydrate polymers and lignin, a complex polymer of phenylpropanoid units (Wright et al., 1988). Lignocellulosic biomass typically contains 55–75% carbohydrates by dry weight (Table 1). Cellulose, like starch, is a polymer of glucose. However, unlike starch, the specific structure of cellulose favors the ordering of the polymer chains into tightly packed, highly crystalline structures that are water insoluble and resistant to depolymerization. The other carbohydrate component in lignocellulosics is hemicellulose, which, dependent on the species, is a branched polymer of glucose or xylose, substituted with arabinose, xylose, galactose, fucose, mannose, glucose, or glucuronic acid. Some of the sidechains may also contain acetyl groups of ferulate (Carpita and Gibeaut, 1993). Hemicellulose hydrogen-bonds to cellulose microfibrils, thus forming a network that provides the structural backbone to plant cell wall. The presence of lignin in some cell walls imparts further strength, and provides resistance against pests and diseases. Cellulose and hemicellulose are potential sources of fermentable sugars (Hinman et al., 1989; Ho et al., 1998; Taherzadeh et al., 1999; Sreenath and Jeffries, 2000). The presence of lignin in the cell wall, however, impedes enzymatic hydrolysis of the carbohydrates.

The crystallinity of cellulose, accessible surface area, protection of cellulose by lignin, the heterogeneous character of biomass particles, and cellulose sheathing by hemicellulose all contribute to the recalcitrance of lignocellulosic biomass to hydrolysis (Rydholm, 1965; Wenzel, 1970; Hsu et al., 1980; Hsu, 1996; Chang and Holtzapple, 2000). However, crystallinity alone is insufficient to prevent significant hydrolysis if sufficient enzyme is used. For example, hydrolysis of Avicel, a microcrystalline cellulose, proceeded to 80% hydrolysis in 6 days when incubated with 72 units of Genencor Cytolase (CL) cellulase per gram (Ladisch et al., 1992). The relationships between structural and compositional factors reflect the complexity of lignocellulosic materials. The variability in these characteristics accounts for the varying digestibility between different sources of lignocellulosic biomass. In principle, an effective pretreatment causes disruption of these barriers so that hydrolytic enzymes can penetrate and cause hydrolysis as illustrated schematically in Fig. 1 and also minimizes degradation by avoiding sugar degradation as illustrated in the sequence of Fig. 2 (Ladisch et al., 1983; Lynd et al., 1991; Holtzapple, 1993; Mosier et al., 1999).

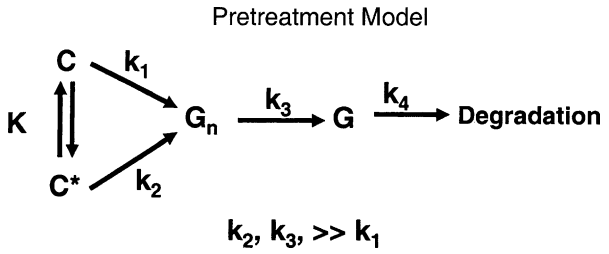

Fig. 2. Schematic representation of pretreatment steps. Transformation between crystalline (C) amorphous cellulose (C*) is reversible. Both forms may yield oligosaccharides, which in turn form glucose. Glucose degradation can then occur to form fermentation inhibitors (from Weil, 1992).

4. Goals of pretreatment

An effective pretreatment is characterized by several criteria. It avoids the need for reducing the size of biomass particles, preserves the pentose (hemicellulose) fractions, limits formation of degradation products that inhibit growth of fermentative microorganism, minimizes energy demands and limits cost (National Research Council, 1999). These properties, along with others including low pretreatment catalyst cost or inexpensive catalyst recycle, and generation of higher-value lignin co-product form a basis of comparison for various pretreatment options. Pretreatment results must be balanced against their impact on the cost of the downstream processing steps and the trade-off between operating costs, capital costs, and biomass costs (Lynd et al., 1996; Wyman, 1995b, 1996, 1999; Delgenes et al., 1996; Palmqvist and Hahn-Hagerdal, 2000; Ladisch et al., 1983). The process itself utilizes pretreatment additives and/or energy to form solids that are more reactive than native material and/or generate soluble oligo- and monosaccharides (Fig. 3). We review pretreatment technologies that have promise for cost effective pretreatment of cellulosic biomass for biological conversion to fuels and chemicals.

5. Pretreatment process economic analysis

Rigorous process economic analysis is necessary to determine the best pretreatment process options for a

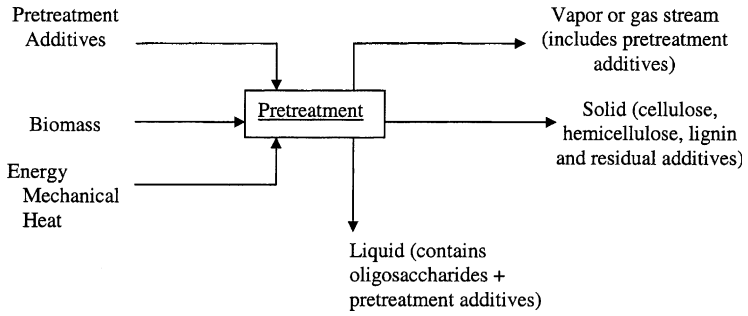

Fig. 3. Schematic of Pretreatment Process.

particular feedstock and product opportunity, once the experimental data are available (Aden et al., 2002). Economic analysis helps to direct research and development efforts by identifying process parameters that have the greatest impact on overall economics. These parameters can be used to benchmark a conceptual process design. The benchmark may then be compared to other cases where key process parameters are systematically varied. The impact of changes in pretreatment on other unit operations, such as the enzymatic digestibility of pretreated solids or the relative toxicity to fermentative microorganisms represent important metrics. Process economic analysis also enable estimation of an absolute production cost for ethanol or other potential products necessary for comparing biorefinery-based costs to existing processes. The combination of experimental data and economic modeling also results in a matrix that matches feedstocks with conversion options, as well as for comparing the impact of pretreatment processes.

Process engineering efforts at the National Renewable Energy Laboratory for ethanol and other chemicals from biomass have led to the development of fully-integrated material balance and financial models based upon the ASPEN PLUS process simulator (AspenTech, Cambridge, MA) (Wooley et al., 1999). These models involve rigorous material and energy balance calculations based upon accepted thermodynamic and physical property data, including a physical property database for biomass materials that has been specifically developed for this purpose (Wooley and Putsche, 1996). Careful mass balances, contingent upon effective analytical methods, track the mass flow for evaluation of the process efficiency. Models are being developed for each of the pretreatment technologies discussed in this paper and will be used to evaluate their current state and ultimate potential.

6. Pretreatment categories

Pretreatment methods are either physical or chemical. Some methods incorporate both effects (McMillan, 1994; Hsu, 1996). For the purposes of classification, steam and water are excluded from being considered chemical agents for pretreatment since extraneous chemicals are not added to the biomass. Physical pretreatment methods include comminution (mechanical reduction in biomass particulate size), 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 through subsequent processing steps. Acids or bases that promote hydrolysis and improve the yield of glucose recovery from cellulose by removing hemicellulose or lignin during pretreatment. The most commonly used acid and base are H_2SO_4 and NaOH, respectively.

Cellulose solvents are another type of chemical additive. Solvents that dissolve cellulose in bagasse, cornstalks, tall fescue, and orchard grass resulted in 90% conversion of cellulose to glucose (Ladisch et al., 1978; Hamilton et al., 1984) and showed enzyme hydrolysis could be greatly enhanced when the biomass structure is disrupted before hydrolysis. Alkaline H_2O_2, ozone, organosolv (uses Lewis acids, $FeCl_3$, $(Al)_2SO_4$ in aqueous alcohols), glycerol, dioxane, phenol, or ethylene glycol are among solvents known to disrupt cellulose structure and promote hydrolysis (Wood and Saddler, 1988). Concentrated mineral acids (H_2SO_4, HCl), ammonia-based solvents (NH_3, hydrazine), aprotic solvents (DMSO), metal complexes (ferric sodium tartrate, cadoxen, and cuoxan), and wet oxidation also reduces cellulose crystallinity and disrupt the association of lignin with cellulose, as well as dissolve hemicellulose. These methods, while effective, are too expensive to be practical when measured against the value of the glucose (approximately 5¢/lb).

The pretreatment methods outlined in Table 1: steam explosion, liquid hot water, dilute acid, lime, and ammonia pretreatments, have potential as cost-effective pretreatments and are discussed in this review. Key features that differentiate approaches are outlined with the discussion following the summary in Table 2.

Table 2
Effect of various pretreatment methods on the chemical composition and chemical/physical structure of lignocellulosic biomass

	Increases accessible surface area	Decrystalizes cellulose	Removes hemicellulose	Removes lignin	Alters lignin structure
Uncatalyzed steam explosion	■		■		▪
Liquid hot water	■	ND	■		▪
pH controlled hot water	■	ND	■		ND
Flow-through liquid hot water	■	ND	■	▪	▪
Dilute acid	■		■		■
Flow-through acid	■		■	▪	■
AFEX	■	■	▪	■	■
ARP	■	■	▪	■	■
Lime	■	ND	▪	■	■

■: Major effect.
▪: Minor effect.
ND: Not determined.

7. Uncatalyzed steam explosion

Uncatalyzed steam explosion is applied commercially to hydrolyze hemicellulose for manufacture of fiberboard and other products by the Masonite process (Mason, 1926; DeLong, 1981). Wood chips are conveyed into large vessels, and high-pressure steam is applied for a few minutes without addition of chemicals. At a set time, some steam is rapidly vented from the reactor to reduce the pressure, and the contents are discharged into a large vessel to flash cool the biomass.

7.1. Process description

Extensive research has been conducted on steam explosion, (see reviews of Saddler et al., 1993; Hsu, 1996; McMillan, 1994). Uncatalyzed steam explosion refers to a pretreatment technique in which lignocellulosic biomass is rapidly heated by high-pressure steam without addition of any chemicals. The biomass/steam mixture is held for a period of time to promote hemicellulose hydrolysis, and terminated by an explosive decompression (Brownell and Saddler, 1984; Avellar and Glasser, 1998; Glasser and Wright, 1998; Heitz et al., 1991; Abatzoglou et al., 1992; Ramos et al., 1992). Hemicellulose is thought to be hydrolyzed by the acetic and other acids released during steam explosion pretreatment. Steam explosion involves chemical effects and a reaction sequence of the type shown in Fig. 2 since acetic acid is generated from hydrolysis of acetyl groups associated with the hemicellulose may further catalyze hydrolysis and glucose or xylose degradation. Water, itself, also acts as an acid at high temperatures (Weil et al., 1997; Baugh et al., 1988a,b).

Steam provides an effective vehicle to rapidly heat cellulosics to the target temperature without excessive dilution of the resulting sugars. Rapid pressure release rapidly reduces the temperature and quenches the reaction at the end of the pretreatment. The rapid thermal expansion used to terminate the reaction opens up the particulate structure of the biomass but enhancement of digestibility of the cellulose in the pretreated solid is only weakly correlated with this physical effect (Brownell et al., 1986; Biermann et al., 1984).

7.2. Mode of action

The major chemical and physical changes to lignocellulosic biomass by steam explosion are often attributed to the removal of hemicellulose. This improves the accessibility of the enzymes to the cellulose fibrils. Reduction in biomass particle size and increased pore volume after explosive decompression is less important in improving the digestibility of steam exploded lignocellulosic biomass.

8. Liquid hot water pretreatments

Water pretreatments use pressure to maintain the water in the liquid state at elevated temperatures (Bobleter, 1994; Bobleter et al., 1976, 1981; Bobleter and Concin, 1979; Hormeyer et al., 1988a,b; Walch et al., 1992; Mok and Antal, 1992; Kohlman et al., 1995; Allen et al., 1996; van Walsum et al., 1996). Flow-through processes pass water maintained in the liquid state at elevated temperatures through cellulosics. This type of pretreatment has been termed hydrothermolysis (Bobleter et al., 1981; Bobleter and Concin, 1979), aqueous or steam/aqueous fractionation (Bouchard et al., 1991), uncatalyzed solvolysis (Mok and Antal, 1992, 1994), and aquasolv (Allen et al., 1996).

Solvolysis by hot compressed liquid water contacts water with biomass for up to 15 min at temperatures of 200–230 °C. Between 40% and 60% of the total biomass is dissolved in the process, with 4–22% of the cellulose, 35–60% of the lignin and all of the hemicellulose being removed. Over 90% of the hemicellulose is recovered as monomeric sugars when acid was used to hydrolyze the resulting liquid. The pretreatment results

were found to be virtually independent of temperature and time. Variability in results was related to the biomass type with high lignin solubilization impeding recovery of hemicellulose sugars (Mok and Antal, 1992, 1994).

There are three types of liquid hot water reactor configurations. Co-current, countercurrent, and flow through (illustrated in Fig. 4). In co-current pretreatments, a slurry of biomass and water is heated to the desired temperature and held at the pretreatment conditions for a controlled residence time before being cooled. Counter-current pretreatment is designed to move water and lignocellulose in opposite directions through the pretreatment reactor. In a flow-through reactor, hot water passed over a stationary bed of lignocellulose hydrolyzes and dissolves lignocellulose components and carries them out of the reactor.

8.1. Process descriptions

Co-current liquid hot water pretreatment is being used to pretreat corn fiber generated by corn-to-ethanol processing for the current fuel ethanol industry (Weil et al., 1998b, Beery et al., 2000; Mosier et al., 2003a,b). Biomass liquid slurry of approximately 16% undissolved solids passes through heat exchangers, is heated to the desired temperature (140–180 °C), (heat exchangers 1 and 2, Fig. 4(a)) and held at temperature for 15–20 min as the slurry passes through an insulated plug-flow, snake-coil. The slurry is cooled and heat recovered by countercurrent heat exchange with the incoming slurry. The resulting pretreated fiber is devoid of starch, and the cellulose is completely digestible in 24 h at enzyme loadings of 20 FPU/gram.

Flow-through technologies pass hot water at 180–220 °C and about 350–400 psig pressure to achieve overall sugar yields of up to 96% but suffer from low concentration of sugars (of about 0.6–5.8 g/L) from hemicellulose. The solids that are left behind have enhanced digestibility and a significant portion of the lignin is also removed. In countercurrent pretreatment the biomass slurry is passed in one direction while water is passed in another in a jacketed pretreatment reactor (Fig. 4(b)). Temperatures, back pressures and residence times are similar. In the flow-through pretreatment reactor water or acid is passed over a stationary bed, and removes some of the biomass components including lignin (Fig. 4(c)).

Water pretreatment reduces the need for neutralization and conditioning chemicals since acid is not added. Size reduction of the incoming biomass is not needed since the lignocellulose particles break apart when cooked in water (Kohlman et al., 1995; Weil et al., 1997). A highly digestible cellulose results when enzyme is added (van Walsum et al., 1996; Weil et al., 1998a,b; Mosier et al., 2003a,b), and high yields of sugars from

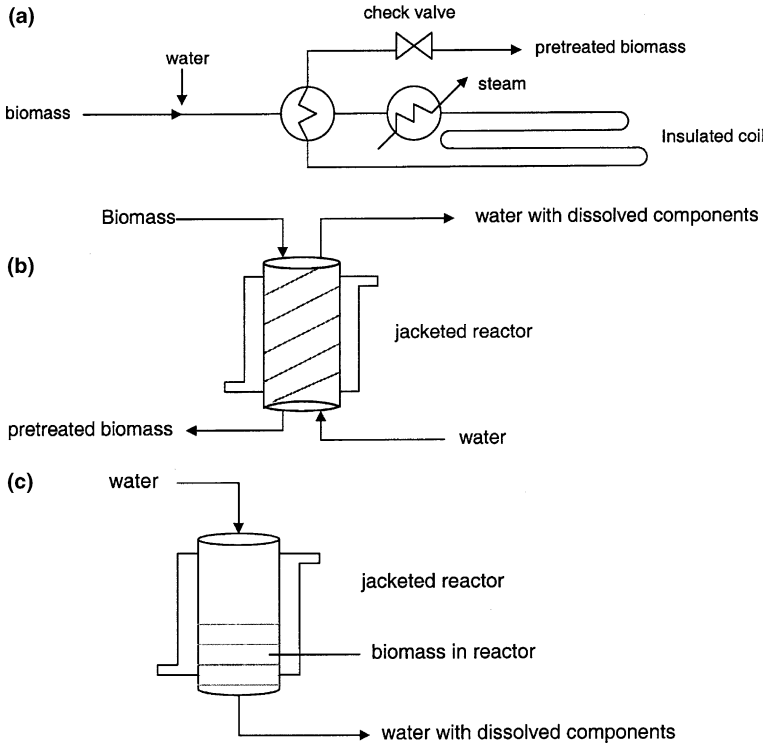

Fig. 4. Schematic illustrations of co-current, counter-current, and flow-through pretreatment methods: (a) Co-current liquid hot water pretreatment, (b) counter-current reactor, (c) flow-through reactor.

hemicellulose occur during pretreatment. The liquid hydrolyzate is fermentable to ethanol (Lynd et al., 1996; van Walsum et al., 1996; Mosier et al., 2003a,b).

8.2. Mode of action

It is likely that structural and chemical changes occur to the lignin in the non flow-through methods. However, the lack of effective analytical methods for evaluating lignin structure and chemical composition has hindered developing an understanding this phenomenon.

Liquid hot water pretreatments are both helped and hindered by the cleavage of *O*-acetyl and uronic acid substitutions from hemicellulose to generate acetic and other organic acids. The release of these acids helps to catalyze formation and removal of oligosaccharides. However, the polysaccharides and especially hemicellulose, may be further hydrolyzed to monomeric sugars which are subsequently partially degraded to aldehydes if acid is used. These aldehydes, principally furfural from pentoses and 5-hydroxymethyl furfural from hexose, are inhibitory to microbial fermentation (Palmqvist and Hahn-Hagerdal, 2000).

The pK_a of water is affected by temperature such that the pH of pure water at 200 °C is nearly 5.0 (Weil et al., 1998a). Water has an unusually high dielectric constant that enables ionic substances to dissociate. Water is able to dissolve all of the hemicellulose. One half to two thirds of the lignin also dissolves from most biomass materials when these materials are treated at 220 °C for 2 min. Hot water cleaves hemiacetal linkages and liberates acids during biomass hydrolysis. This facilitates the breakage of such ether linkages in biomass (Antal, 1996). Softwoods are less susceptible to solubilization for reasons that are not well understood.

The control of pH during pretreatment of Avicel® and other types of lignocellulose using potassium hydroxide, to prevent the pH of the liquid hot water from falling below 4 limits and/or controls the chemical reactions occurring during pretreatment (Kohlman et al., 1995). The base differs in function from chemicals added as catalysts in chemical pretreatment methods with its role to maintain the pH constant above 5 and below 7 in order to minimize hydrolysis to monosaccharides (Weil et al., 1998a).

9. Acid pretreatment

Acid pretreatment has received considerable research attention over the years, with reviews given by Tsao et al. (1982), Bienkowski et al. (1984), McMillan (1994), Hsu (1996), Jacobsen and Wyman (1999), and Lee et al. (1999). Dilute sulfuric acid has been added to cellulosic materials for some years to commercially manufacture furfural (Root et al., 1959; Zeitsch, 2000). Dilute sulfuric acid is mixed with biomass to hydrolyze hemicellulose to xylose and other sugars and then continue to break xylose down to form furfural. The furfural is recovered by distillation. The volatile fraction contains the furfural which is purified and sold. The acid is mixed or contacted with the biomass, and the mixture is held at temperatures of 160–220 °C for periods ranging from minutes to seconds.

Addition of sulfuric acid has been initially applied to remove hemicellulose either in combination with breakdown of cellulose to glucose or prior to acid hydrolysis of cellulose (Ruttan, 1909; Faith and Hall, 1944; Sherrard and Kressman, 1945; Harris et al., 1945; Faith, 1945; Harris and Begliner, 1946). Hemicellulose is removed when sulfuric acid is added and this enhances digestibility of cellulose in the residual solids (Knappert et al., 1981; Brownell and Saddler, 1984; Converse and Grethlein, 1985; Grous et al., 1985). The most widely used and tested approaches are based on dilute sulfuric acid (Grohmann et al., 1985; Torget et al., 1992; Nguyen et al., 2000; Kim et al., 2000). However, nitric acid (Brink, 1993, 1994), hydrochloric acid (Israilides et al., 1978; Goldstein et al., 1983; Goldstein and Easter, 1992), and phosphoric acid (Israilides et al., 1978) have also been tested.

9.1. Process description

The mixture of acid and biomass can be heated indirectly through the vessel walls or by direct steam injection, the latter being operated in virtually the same manner as for uncatalyzed steam explosion. The acid is added to the liquid percolated through a bed, sprayed onto the residue after which the residue is heated, or agitated with the biomass in a reactor. The reactor configurations are analogous to those of Fig. 3.

Dilute sulfuric acid has some important limitations including corrosion that mandates expensive materials of construction. The acid must be neutralized before the sugars proceed to fermentation. Gypsum has problematic reverse solubility characteristics when neutralized with inexpensive calcium hydroxide. Formation of degradation products and release of natural biomass fermentation inhibitors are other characteristics of acid pretreatment. Disposal of neutralization salts (Hinman et al., 1992; Wooley et al., 1999; US Department of Energy, 1993; Hsu, 1996; McMillan, 1994; Grohmann et al., 1985, 1986; Torget et al., 1991; Forsberg et al., 1986; Mes-Hartree and Saddler, 1983), as well as a 7-day reaction time with cellulase loadings of up to 20 IFPU/gram cellulose translate into added cost (Wright et al., 1987; Hinman et al., 1992; US Department of Energy, 1993; Wooley et al., 1999). Grinding of the cellulose to 1 mm accounts for 33% of the power requirements of the entire process (Hinman et al., 1992; US Department of Energy, 1993; Wooley et al., 1999).

Nitric acid reduces containment costs relative to sulfuric (Brink, 1993, 1994), but the higher acid cost counterbalances this benefit.

Use of acid to remove hemicellulose has been tried on a wide range of feedstocks ranging from hardwoods to grasses and agricultural residues (Knappert et al., 1981; Converse and Grethlein, 1985; Grous et al., 1985; Lee et al., 1978; Grohmann et al., 1985; Torget et al., 1990, 1991, 1992). Most species performed well, and corn cobs and stover were found to be particularly well suited to pretreatment by hemicellulose hydrolysis (Torget et al., 1991). Pretreatment of aspen wood and wheat straw were studied at higher solids concentrations of 20–40% in test tubes heated in an aluminum block for temperatures of 140 and 160 °C (Grohmann et al., 1986). Sulfuric acid levels of 0.45–0.85% were used for aspen to reduce the pH to about 1.1–1.5, but up to 2.0% acid was needed to compensate for the neutralizing ability of wheat straw. The use of acid to hydrolyze oligomers released during uncatalyzed hydrolysis results in close to complete hydrolysis to monosaccharides but also the formation of aldehydes (Garrote et al., 2001; Shevchenko et al., 2000).

9.2. Mode of action

Acid hydrolysis releases oligomers and monosaccharides and has historically been modeled as a homogeneous reaction in which acid catalyzes breakdown of cellulose to glucose followed by breakdown of the glucose released to form HMF and other degradation products (Saeman, 1945). This reflects the approximately equal reactivity of glycosidic bonds in these polymers with respect to hydrolysis. Various researchers adapted Saeman's kinetics to describe the hydrolysis of hemicellulose and formation of furfural and other decomposition products (Kwarteng, 1983; Kim and Lee, 1987; Ladisch, 1989; Converse et al., 1989; Esteghlalian et al., 1997; Lee et al., 1999; Mosier et al., 2002).

Oligomers are generally ignored in many models since they are viewed as being too short-lived to be important (Ranganathan et al., 1985; Bhandari et al., 1984; Maloney et al., 1985). Others have shown oligomers to be present in batch hydrolysis systems (Kim and Lee, 1987) and to be a significant fraction of the product for very dilute acid and water only flow-through systems (Bobleter et al., 1981; Mok and Antal, 1992; Bobleter, 1994; Allen et al., 1996; Torget et al., 1996). Kinetic models have been modified to include hemicellulose hydrolysis to oligomers followed by their breakdown to sugars where the sugars degrade to furfural and other compounds for batch, percolation, and flow-through dilute acid-catalyzed systems (Chen et al., 1996). Modeling of hemicellulose hydrolysis as a biphasic reaction incorporates fast and slow hydrolyzing solid hemicellulose fractions (Kobayashi and Sakai, 1956; Grohmann et al., 1985; Maloney et al., 1985; Chen et al., 1996).

Improvements have also been realized by adding additional acid to compensate for the capacity of minerals in the substrate to neutralize some of the acid (Kwarteng, 1983; Esteghlalian et al., 1997; Cahela et al., 1983; Conner et al., 1986) and by calculating the hydrogen ion concentration from the pH (Malester et al., 1992). The influence of pH on rate has been factored into kinetic models to predict that the sugar yields will be highest in a pH range of 2.0–2.5 (Baugh et al., 1988a,b).

10. Flow-through acid pretreatment

Addition of very dilute sulfuric acid (about 0.07% versus the 0.7–3.0% typical for the dilute acid technology described) in a flow-through reactor configuration is effective at acid levels lower than 0.1%. Lower temperatures were applied to hydrolyze the more reactive hemicellulose in yellow poplar in a countercurrent flow-through pretreatment. A more severe condition then hydrolyzed the more recalcitrant hemicellulose fraction.

10.1. Process description

Fresh acid/water stream is first passed through the higher temperature zone and then the lower temperature region to reduce the exposure of sugars to severe conditions and improve yields. Temperatures of 140, 150, and 174 °C were studied for the first stage while the second stage was run at 170, 180, 190, 200, and 204 °C. Times of 10, 15, and 20 min were used in each with sulfuric acid levels of 0.0735%, 0.4015%, and 0.735% by weight. From 83.0 to essentially 100% of the hemicellulose and 26.3–52.5% of the lignin was solubilized, with from 95.2% to 79.6% of the hemicellulose being sugar monomers and the remainder being oligomers. The pretreated cellulose was highly digestible upon subsequent enzyme hydrolysis with up to 90% being attained (Torget et al., 1996, 1998, 1999).

Despite achieving excellent hemicellulose sugar yields and highly digestible cellulose with low acid loadings, equipment configurations and the high ratio of water to solids employed in flow-through systems require significant energy for pretreatment and product recovery. Practical systems that lend themselves to commercial applications have not been demonstrated.

11. Lime pretreatment

Alkali pretreatment processes utilize lower temperatures and pressures compared to other pretreatment technologies. Alkali pretreatment may be carried out at ambient conditions, but pretreatment time is meas-

ured in terms of hours or days rather than minutes or seconds. Unlike acid-catalyzed pretreatments, a limitation occurs because some of the alkali is converted to irrecoverable salts or incorporated as salts into the biomass by the pretreatment reactions. Lime has been used to pretreat wheat straw (85 °C for 3 h, Chang et al., 1998), poplar wood (150 °C for 6 h with 14-atm oxygen, Chang et al., 2001), switchgrass (100 °C for 2 h, Chang et al., 1997), and corn stover (100 °C for 13 h, Karr and Holtzapple, 1998, 2000).

Playne (1984) treated sugarcane bagasse with lime at ambient conditions for up to 192 h to improve the enzyme digestibility of the cellulose from 20% before pretreatment to 72% after pretreatment. Higher temperatures and shorter reactions times were also shown to effectively pretreat lignocellulose with lime. Chang et al. (1998), obtained similar digestibility results by pretreating bagasse with lime at 120 °C for 1 h. Other alkali pretreatments use sodium, potassium, calcium, and ammonium hydroxide as reactants. Sodium hydroxide has received the most attention (Sharmas et al., 2002; Soto et al., 1994; Fox et al., 1989; MacDonald et al., 1983). Lime (calcium hydroxide) has the additional benefits of low reagent cost and safety (Chang et al., 1997; Playne, 1984) and being recoverable from water as insoluble calcium carbonate by reaction with carbon dioxide. The carbonate can then be converted to lime using established lime kiln technology (Chang et al., 1998).

The addition of air/oxygen to the reaction mixture greatly improves the delignification of the biomass, especially highly lignified materials such as poplar (Chang and Holtzapple, 2000). Oxidative lime pretreatment of poplar (Chang et al., 2001) at 150 °C for 6 h removed 77.5% of the lignin from the wood chips and improved the yield of glucose from enzymatic hydrolysis from 7% (untreated) to 77% (treated) compared to the untreated and pretreated poplar wood.

11.1. Process description

The process of lime pretreatment involves slurrying the lime with water, spraying it onto the biomass material, and storing the material in a pile for a period of hours to weeks. The particle size of the biomass is typically 10 mm or less. Elevated temperatures reduce contact time (i.e., 3 h at 85 °C for wheat straw and 13 h at 100 °C for corn stover).

11.2. Mode of action

Alkali pretreatment technologies, including lime pretreatment, are rather similar to the Kraft paper pulping technology. The major effect of the alkaline pretreatment is the removal of lignin from the biomass, thus improving the reactivity of the remaining polysaccharides. In addition, alkali pretreatments remove acetyl and the various uronic acid substitutions on hemicellulose that lower the accessibility of the enzyme to the hemicellulose and cellulose surface (Chang and Holtzapple, 2000).

For lesser ligninified materials such as corn stover, the addition of oxygen appears to only marginally improve the digestibility of pretreated corn stover with lime at a 1:0.075 ratio (stover:lime) at 120 °C for times up to 6 h, (Karr and Holtzapple, 1998). Corn stover pretreated for the optimal time (4 h) at 120 °C loses 32% of the lignin. Hydrolysis yielded 88% of the cellulose as glucose after 7 days at an enzyme loading of 25 FPU per gram of biomass.

12. Ammonia pretreatment

Ammonia fiber/freeze explosion (AFEX) pretreatment yields optimal hydrolysis rates for pretreated lignocellulosics with close to theoretical yields at low enzyme loadings (<5 FPU per gram of biomass or 20 FPU/g cellulose) (Dale, 1986; Dale and Moreira, 1982; Holtzapple et al., 1991; Dale et al., 1996; Moniruzzaman et al., 1997; Foster et al., 2001). Herbaceous and agricultural residues are well suited for AFEX. However, this method works only moderately well on hardwoods, and is not attractive for softwoods (McMillan, 1994).

12.1. Process description

Pretreatment with aqueous ammonia in a flow-through mode involves putting ammonia solution (5–15%) through a column reactor packed with biomass at elevated temperatures (160–180 °C) and a fluid velocity of 1 mL/cm^2 min with residence times of 14 min. This method is also known as ammonia recycled percolation (ARP) process since ammonia is separated and recycled. Under these conditions, aqueous ammonia reacts primarily with lignin (but not cellulose) and causes depolymerization of lignin and cleavage of lignin-carbohydrate linkages. A large and adjustable degree of delignification has been reported in tests with hardwood (Yoon et al., 1995) and agricultural residues (Iyer et al., 1996) at 160–180 °C with residence times at 14 min. It was somewhat less efficient in pretreatment of softwood-based pulp mill sludge (Kim et al., 2000).

Modification of the process was attempted to further increase the extent of the delignification and to achieve fractionation of biomass (Kim and Lee, 1996; Kim et al., 2002). Since lignin is one of the key factors affecting the enzymatic hydrolysis (Dunlap et al., 1976; Mooney et al., 1998; and Lee and Yu, 1995), removal of lignin lowers the enzyme requirement. A recent study reported the enzymatic digestibility of the ammonia recycled percolation treated corn stover to be 90% with an enzyme loading of 10 FPU/g-glucan which is higher than that required for α-cellulose (Kim et al., 2002).

12.2. Mode of action

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 the cellulases to the cellulose. Liquid ammonia causes cellulose swelling and a phase change in the crystal structure from cellulose I to cellulose III. It is believed that ammonlolysis of glucuronic cross-links make the carbohydrate more accessible (Lin et al., 1981).

The cost of ammonia and especially of ammonia recovery drives the cost of this pretreatment (Holtzapple et al., 1992). However, biomass pretreatment economics are also strongly influenced by total sugar yields achieved, and by the loss in yield and inhibition of downstream processes caused by sugar degradation products. The moderate temperatures (<90 °C) and pH values (<12.0) of the AFEX treatment minimize formation of sugar degradation products while giving high yields.

13. Conclusions

Cellulose crystallinity, accessible surface area, protection by lignin, and cellulose sheathing by hemicellulose all contribute to its resistance of biomass to enzymatic hydrolysis. The various pretreatment technologies reviewed above affect at least two of these chemical/physical factors (Table 1). The development of advanced pretreatment technologies that control mechanisms, are tuned to unique characteristics of different types of biomass and minimize cost are still needed. The ultimate goal is the efficient fractionation of lignocellulose into multiple streams that contain value-added compounds in concentrations that make purification, utilization, and/or recovery economically feasible. Greater fundamental understanding of the chemical and physical mechanisms that occur during pretreatment along with an improved understanding of the relationship between the chemical composition and physico-chemical structure of lignocellulose on the enzymatic digestibility of cellulose and hemicellulose is required for the generation of effective pretreatment models. Predictive pretreatment models will enable the selection, design, optimization, and process control pretreatment technologies that match biomass feedstock with the appropriate method and process configuration.

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