6

Fundamentals of Biomass Pretreatment at Low pH

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6.1 Introduction

A wide variety of conversion processes can be used to generate fuels and chemicals from biomass, with many including a hydrolysis and/or dehydration reaction at low pH as an initial stage. In the case of acid hydrolysis of biomass prior to enzymatic hydrolysis and fermentation, this step is called pretreatment. Due to the diversity of conversion processes, it is difficult to define a single set of objectives; the general goals however are to generate reactive intermediates in high yields for subsequent conversion to final products and minimize generation of compounds that interfere with downstream operations. For example, if lignocellulosic biomass is to be converted to ethanol through dilute acid pretreatment, enzymatic hydrolysis, and fermentation, the objectives of pretreatment are to produce high yields of hemicellulose sugars, improve the enzymatic digestibility of the remaining solids to realize high yields of glucose, and avoid generating biological inhibitors such as furfural and acetic acid. On the other hand, if lignocellulosic biomass is to be converted into jet fuel alkanes through cellulose hydrolysis to levulinic acid followed by catalytic processing of levulinic acid to alkanes, the objectives are to generate levulinic acid in high yields and avoid solid catalyst poisons such as mineral acids.

Two of the primary advantages of low-pH reactions are the ready availability of catalysts such as H_2SO_4 and SO_2 and high product yields. However, the capital costs of reactors and associated equipment used for low-pH reactions are high due to the need for expensive, corrosion-resistant materials. In addition, the solid and liquid streams resulting from low-pH pretreatment often require washing or neutralization. Both of

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these considerations create technical challenges and add cost. Finally, the conditioning process to reduce inhibitors can result in sugar losses as well as added expense. For example, Martinez *et al.* [1] found that the total sugars in pretreatment hydrolysate decreased by $8.74 \pm 4.46\%$ after overliming.

This chapter will first explore the earliest use of acid in biomass conversion that provided a foundation for extension to biological conversion of biomass to ethanol, that is, pretreatment: cellulose hydrolysis to glucose for fermentation to ethanol. Examples of the operating conditions associated with this process will be presented. Emphasis will be placed on the use of SO_2 and H_2SO_4, the most common acidifying agents, given their effectiveness and low price. Dilute acid pretreatments are now evolving to support conversion of biomass to hydrocarbon fuels with solid catalysts. Kinetic models of cellulose and hemicellulose hydrolysis at low pH conditions will also be presented. One model of pretreatment makes use of a relationship known as the combined severity (CS) factor, defined as [2,3]:

$$\log(\text{CS}) = \log\left[t \exp\left(\frac{T - 100}{14.75}\right)\right] - \text{pH} \tag{6.1}$$

where *t* is the time in minutes, and *T* is the temperature in degrees Celsius. This relationship will be discussed in further detail as a useful way of comparing the different pretreatment conditions presented.

Low-pH pretreatment is a diverse field, the references to which could easily fill a book. Therefore, the objective of this chapter is to provide a summary along with key references for the interested reader to pursue for more details. The selection of pretreatment conditions is a complex problem that depends on factors such as process objectives, biomass species, chemical costs, safety considerations, and local influences such as regulations or chemical availability. It is currently not possible to identify optimum pretreatment conditions without extensive experimental work and process engineering to arrive at the optimal overall system.

6.2   Effects of Low pH on Biomass Solids

6.2.1   Cellulose

Cellulose is a linear polymer of glucose that typically accounts for 35–50% of lignocellulosic biomass [4]. The monomer units are covalently linked by 1,4-glycosidic bonds [5]. Due to the presence of multiple hydroxyl groups, there is a high degree of intramolecular and intermolecular hydrogen bonding between the glucan chains [5]. The glucan chains form a crystalline core with a semi-crystalline shell [6,7].

Due to the crystalline nature of cellulose, very low pH, high temperatures, or extended times are required to hydrolyze significant quantities of cellulose to glucose [8]. Under conditions that favor cellulose hydrolysis, the glucose released degrades to products such as levulinic and formic acid [8]. Under less severe hydrolysis conditions, the degree of polymerization has been found to change substantially. Several researchers [9–11] hydrolyzed different cellulose substrates such as cotton linters and wood pulp with 2.45–5 M HCl or 2.5 M H_2SO_4 at 5–105 °C for 0.25–480 hours and then calculated the degree of polymerization from cuprammonium viscosity values. These treatments resulted in 2–20% loss of cellulose. They found that during hydrolysis the degree of polymerization decreased rapidly initially and then stabilized at a level-off degree of polymerization (LODP), with the time to reach the LODP typically 15–30 minutes [9–11]. It was proposed that the initial decrease in degree of polymerization (DP) was due to the rapid hydrolysis of amorphous cellulose. Nickerson and Habrle found that H_2SO_4 had similar hydrolytic effects as HCl [11]. In his study, Battista subjected wood pulp to mild hydrolysis with 5 M HCl at 18 °C for 24 hours to 44 weeks, a drastic hydrolysis with boiling 2.5 M HCl for 1–15 minutes, or mild hydrolysis followed by drastic hydrolysis [9]. In this case, the weight loss during drastic hydrolysis for the sequential process was lower than the weight loss for the single-stage drastic hydrolysis [9]. Based on these

observations Battista proposed that, under mild conditions, hydrolysis occurs slowly and crystallization generates pieces that are more resistant to acid hydrolysis [9]. A study by Bouchard *et al.* revealed similar trends in the degree of polymerization following hydrolysis of α-cellulose; they also showed that after a period of slow depolymerization, the rate of depolymerization increased [12]. These three phases were attributed to endogenous attack of amorphous cellulose by acid followed by exogenous acid attack of the ends of crystalline cellulose, and finally simultaneous endogenous/exogenous hydrolysis of the remaining cellulose. Changes in the degree of polymerization of cellulose in lignocellulosic materials following acid hydrolysis have also been detected. Martínez and colleagues subjected a softwood mixture and almond shells to dilute acid pretreatment and then determined the degree of polymerization from intrinsic viscosity measurements [13]. When Martínez *et al.* plotted the degree of polymerization as a function of severity, they observed the characteristic rapid decrease in degree of polymerization for both substrates [13]. In the case of a softwood mixture, this rapid initial decrease was followed by stabilization at the level-off degree of polymerization [13]. Almond shells were not pretreated at high severity conditions, so no LODP was observed [13]. Kumar *et al.* subjected corn stover and poplar to hydrolysis with dilute H_2SO_4 and SO_2 [14]. These treatments removed 3.1–12.1% of the glucan in biomass and reduced the degree of polymerization by 65–85% compared to untreated biomass [14]. The degree of polymerization of cellulose in switchgrass has also been shown to decrease following pretreatment with $0.1 \, mol/m^3$ H_2SO_4 at 160 °C [15].

Mild hydrolysis has also been found to affect biomass crystallinity. In work by Kumar *et al.*, the crystallinity index of the pretreated materials was measured by wide-angle X-ray diffraction and Fourier transform infrared attenuated total reflectance (FTIR-ATR) [14]. The X-ray diffraction measurements showed that the crystallinity index of corn stover and poplar increased while the FTIR spectra indicated that the ratio of amorphous to crystalline cellulose decreased [14]. The increase in crystallinity index may therefore reflect removal of amorphous components such as hemicellulose and lignin from biomass and not an increase in cellulose crystallinity.

6.2.2   Hemicellulose

The second-most plentiful carbohydrate fraction in most lignocellulosic biomass is hemicellulose. Hemicellulose typically accounts for approximately 15–35% of biomass [4]. For hardwoods, grasses, and agricultural residues, hemicellulose polymers primarily consist of pentose sugars such as xylose and arabinose. Depending on the substrate, hemicellulose typically also contains the hexose sugars glucose, mannose, and galactose, with these sugars being most prevalent in softwoods. The structure of hemicellulose is more complex than cellulose and contains many branches. Acetyl is the most common side group [4].

Due to its branched structure, hemicellulose is amorphous and much more susceptible to hydrolysis by acids than cellulose. In fact, hemicellulose can be almost completely removed with limited damage to cellulose [16]. The extent of hemicellulose removal, of course, depends upon hydrolysis conditions. For example, Öhgren *et al.* were able to recover approximately 65% of the xylan in corn stover hydrolysates following pretreatment with 2% SO_2 at 200 °C for 2 minutes, while only an 18% yield was achieved with the same corn stover pretreated at 170 °C for 2 minutes with 2% SO_2 [17].

The removal of hemicellulose appears to depend upon the acidifying agent. For example, Martín *et al.* found that pretreatment of sugarcane bagasse with H_2SO_4 resulted in complete removal and partial degradation of xylan, while SO_2 pretreatment removed less xylan but produced substantially fewer degradation products such as furfural [18]. These differences were likely due to the differences in the amount of H_2SO_4 or SO_2 absorbed by bagasse prior to pretreatment.

Hemicellulose sugars can be released into solution either as oligomers or monomers, with their ratios varying with temperature, time, and acid concentration. For example, as the temperature was increased from 201 °C to 225 °C for hydrolysis of poplar in 0.4% H_2SO_4, the fraction of monomers in the hydrolysate

increased from 55 to 76% [19]. In another study, increasing the H_2SO_4 concentration increased the selective production of xylose from xylooligomers [20].

Acetyl groups are removed during acid hydrolysis as acetic acid or attached to solubilized hemicellulose [16,20,21]. Experimental results indicate that once released, acetic acid does not degrade [16,21,22]; increasing hydrolysis time therefore increases the release of acetyl monomers from hemicellulose. However, there is no consensus on the effect of temperature on the release of acetyl groups. For example, Maloney *et al.* found that the acetyl removal rate from paper birch was slightly faster than that of xylan removal at 100 and 130 °C but decreased at 150 and 170 °C [21]. In contrast, Aguilar *et al.* showed that increasing the temperature of hydrolysis of sugar cane bagasse from 100 to 122 °C with 2–6% H_2SO_4 increased the acetic acid concentration in the hydrolysate, but a second temperature increase to 128 °C reduced the acetic acid concentration slightly [16]. These differences may be a reflection of differences in the types of biomass used or the acid concentration.

Once in solution, hemicelluloses-derived oligomers can react to form products such as furfural that can react with each other or with sugars to form more complex products [23]; for example, pentose can be acetalized by furfural [24]. Furfural can further decompose to formic acid or humin char [25]. Possible reaction schemes were described by Antal *et al.* [23], Hoydonckx *et al.* [24], and Weingarten *et al.* [25]. These decomposition reactions have been observed for numerous types of biomass including corn stover [17,26], hardwoods [27], softwoods [27], and switchgrass [27]. As hydrolysis time increases, the extent of these decomposition reactions also increases. The higher the hydrolysis temperature, the sooner decomposition becomes significant. For example, the maximum xylose production from corn stover was achieved in 2 minutes at 180 °C and 5 minutes at 160 °C using 0.98% H_2SO_4; for reactions lasting longer than these times, xylose yields dropped due to degradation [26]. Similarly, as acid concentration is increased at a constant temperature, the time to maximum xylose yield or onset of significant degradation drops [26].

6.2.3 Lignin

Lignin is the third major polymer in biomass but is made up of phenol monomers, not sugars. It typically accounts for 17–33% of a plant's mass [28]. Coumaryl, coniferyl, and sinapyl alcohol are the three monomeric precursors to lignin [28]; the relative portions of each monomer vary by biomass species. Lignin's structure is highly irregular and frequently forms covalent bonds with the surrounding carbohydrates, especially hemicellulose [28].

Lignin removal during acid hydrolysis in batch reactors is typically low regardless of biomass type or acidifying agent [14,22,29]. Liu and Wyman found that pumping 0.05–0.1 w/w% H_2SO_4 through corn stover at 180 °C increased lignin removal from approximately 10% in a batch reactor to about 50% [30]. The removal of lignin is accompanied by the generation of aromatic monomers in the liquid hydrolysate, and the type and amount of phenols varies with both the biomass treated and hydrolysis conditions [31]. For example, salicylic acid was found in higher concentrations in hydrolysates produced from poplar than from corn stover and pine, and its concentration varied with H_2SO_4 concentration [31]. Other researchers who identified aromatics in hydrolysates include Martín *et al.* and Excoffier *et al.* [18,19].

The limited removal of lignin from biomass during acid hydrolysis may be somewhat deceiving as it has been shown that the carbohydrate fractions can react to form compounds that analysis procedures measure as lignin. For example, NMR analysis of loblolly pine hydrolyzed at 200 °C with sulfuric, phosphoric, or trifluoroacetic acid ($C_2HF_3O_2$) by Sievers *et al.* displayed an increase in signal intensities associated with aromatic carbon, an increase that could only result from reaction of carbohydrates to aromatics or "pseudo-lignin" [32]. Ritter and Kurth [33] provided further evidence of pseudo-lignin formation from carbohydrates by subjecting poplar-derived holocellulose to acid hydrolysis. Sannigrahi *et al.* [34] recovered

holocellulose, the hemicellulose and cellulose portion of *Populus trichocarpa x deltoids*, by exposing the biomass to $NaClO_2$ and acetic acid twice at 70 °C for one hour. After acid hydrolysis of this holocellulose, a lignin-like fraction, "pseudo-lignin," was detected in the resulting solids by wet chemistry, NMR, and FTIR [33]. However, because the untreated holocellulose contained only 1.6% Klason lignin, the pseudo-lignin was primarily generated through acid-catalyzed reactions of cellulose and hemicellulose [33]. The increased production of pseudo-lignin with increasing hydrolysis severity suggests that researchers should use multiple analytical procedures when determining lignin removal following high-severity hydrolysis.

The lignin that remains in solids following acid hydrolysis is modified in several ways. At a chemical level, researchers have found evidence of acid condensation and oxidation through FTIR [14,29] and decreased bromination [29]. Microscopic examination of the solids following pretreatment revealed dramatic changes in the morphology and distribution of lignin. A number of researchers observed deposition of spherical droplets on cell walls. These droplets were observed to cluster near ultrastructural features such as cell corners [35,36] and demonstrated to contain lignin with a number of techniques including $KMnO_4$ staining [35,36], FTIR spectroscopy [36], NMR analysis [36], and antibody labeling [36]. The morphology and localization of these droplets to the natural pores of biomass led to speculation that a cycle of melting and coalescing may be responsible for lignin removal [35–37].

6.2.4 Ash

Biomass also contains inorganic material, commonly referred to as ash [38], and includes both plant structural components and inorganic materials such as in soil picked up in harvesting operations. In woody species, the structural mineral content ranges from 0.3 to 2 w/w%, while in herbaceous species and agricultural residues, the structural mineral content may account for as much as 16 w/w% [4]. The composition of this inorganic fraction varies by biomass species. Biomass cations include potassium, calcium, magnesium, sodium, manganese, and ammonium; possible anions are sulfates, phosphates, chloride and nitrate [22,39–41]. When combined with biomass, mineral acids such as H_2SO_4 are neutralized through an ion-exchange reaction between inorganic cations and hydronium ions [39]. It is difficult to determine the neutralizing capacity of biomass, but the mineral content provides an adequate estimate [39]. Due to their higher mineral content, the neutralizing capacity of herbaceous biomass and agricultural residues is generally higher than that of woody materials [42,43]. In order to simplify reaction kinetic models, it is frequently assumed that neutralization is instantaneous upon mixing of biomass and acid [22,42,43]. However, Springer and Harris demonstrated that neutralization is in fact a complex phenomenon in that the exchange of cations with hydronium ions varies with temperature and applied acid concentration, and is incomplete even under severe hydrolysis [39].

6.2.5 Ultrastructure

The ultrastructure of biomass undergoes several changes during acid hydrolysis as well. It has been shown that biomass particle sizes decrease during acid hydrolysis and that, as the severity of the treatment increases, the percentages of small particles and fines increase [44]. Additionally, it has been shown that the size of intraparticle pores changes as a result of acid hydrolysis. When Grethlein hydrolyzed birch, maple, poplar, white pine, and steam-extracted southern pine with 1% H_2SO_4 at 180–220 °C for 7.8 seconds, he found that the pore volume increased with increasing pretreatment temperature [45] and attributed these changes in hemicellulose to removal during pretreatment [45]. Excoffier *et al.* and Wong *et al.* saw a similar increase in pore volume with increasing hemicellulose removal [19,46]. However, both groups also indicated that partial removal of cellulose or lignin redistribution might also contribute to changes in pore volume [19,46].

6.2.6   Summary of Effects of Low pH on Biomass Solids

The effects of aqueous, low-pH conditions on biomass ultimately depend on the concentration of the acidifying agent, temperature, and time of the reactions. In general, low-pH aqueous treatments produce biomass solids enriched in cellulose and lignin. Some pseudo-lignin formed from hemicellulose may also be included. The acidic liquid stream or hydrolysate produced contains hemicellulose-derived sugars such as xylose and xylooligomers and associated degradation products such as furfural. Some aromatic monomers derived from lignin may also be detected in the hydrolysate. Although glucose concentrations are generally low for typically favored pretreatment conditions, the amounts of glucose and cellulose degradation products in the hydrolysate will increase as the severity of the reaction conditions is increased.

6.3   Pretreatment in Support of Biological Conversion

6.3.1   Hydrolysis of Cellulose to Fermentable Glucose

Sherrard and Kressman [47] describe how Braconnot discovered the hydrolysis of cellulose to glucose by concentrated acid in 1819. Much of the early work focused on using concentrated acids, such as 40–42% HCl [47] at atmospheric pressure, but in the late nineteenth century Simonsen erected an experimental plant in which cellulose hydrolysis was conducted with 0.5% H_2SO_4 at a pressure of 9 atm ($T_{sat} = 176\,°C$) for 15 minutes [47]. Work was also conducted using sulfurous acid, H_2SO_3, as the hydrolyzing agent. Although a number of similar facilities were constructed during the early twentieth century, these facilities did not operate for long due to numerous technical and commercial difficulties, and ultimately alcohol production from wood was abandoned.

During World War II the demand for ethanol skyrocketed. As the traditional raw material of industrial molasses was scarce, producers began using feedstocks such as wheat flour, corn, sorghum grain, and barley. However, these feedstocks became increasingly difficult to obtain by approximately 1943, so the Chemical Referee Board of the Office of Production Research and Development, War Production Board, recommended that ethanol production from wood be investigated, leading to some of the earliest pretreatment research. These early pretreatments were directed at hemicellulose removal prior to further acid hydrolysis of cellulose to recover 6-carbon sugars for fermentation to ethanol by *Sacchromocyes cerevisiae* [4]. Many of the conditions were selected for complete hydrolysis of cellulose to glucose while allowing pentose degradation, because pentoses were non-fermentable by the available organisms and considered waste [5].

One of the first commercial processes for conversion of cellulosic biomass to ethanol was the Scholler process. Sawdust and wood chips were loaded into brick-lined steel percolators and preheated to 129 °C by steam injection; batches of 0.5% H_2SO_4 were forced through at 1.14–1.24 MPa, as described by Faith [48]. Each batch reaction took approximately 45 minutes [48]. The Madison wood sugar process was a modification of the Scholler process with Douglas fir wood waste first treated with 0.5–0.6% H_2SO_4 at 150 °C for 20 minutes [49]. Additional dilute acid was added as the temperature was increased to 185 °C [49], and the reactor was maintained at this temperature until the completion of the run, typically 2.3–3.0 hours [49]. The resulting sugar solution was continuously removed, and the reducing sugar yields ranged from 35.0% to 49.0% of the theoretical possible maximum [49].

Sulfuric acid was used in both of these commercial examples, but other catalysts were investigated for the complete conversion of cellulose to glucose. Table 6.1 outlines some of the conditions tested. These catalysts were evaluated based on the rate of hydrolysis of cellulose relative to the rate of decomposition of hexose. Phosphoric acid was determined to be a poor catalyst due to the slow rate of hydrolysis and the increase in the rate of glucose degradation [50]. Sulfur dioxide was also found to be a poor catalyst for the hydrolysis of cellulose due to its relatively slow hydrolysis rate [51]. Sulfuric acid and hydrochloric acid

Table 6.1   *Selected conditions for the hydrolysis of cellulose to glucose.*

Agent	Concentration (w/w%)	Temperature (°C)	Time (min)
HCl (Harris and Kline [51])	0.2–3.2	160–190	10–320
H_3PO_4 (Harris and Lang [50])	0.2–3.2	180–195	10–180
SO_2 (Harris and Kline [51])	0.75–3.00	150–180	Various
H_2SO_4 (Harris and Kline [51])	0.04–0.16	170–190	Various
H_2SO_4 (Saeman [86])	0.4–1.6	170–190	0–90

catalysts increased the yields of reducing sugars [51]. Hydrofluoric acid, in both the liquid and vapor phase, was also considered as a catalyst for the production of glucose from lignocellulose [52,53]. Although high yields of glucose were achieved at ambient temperatures and pressures, the hazards and costs of working with hydrofluoric acid on a commercial scale limited interest and research [54].

6.3.2   Pretreatment for Improved Enzymatic Digestibility

Concerns about military equipment rotting in the South Pacific during World War II led to the discovery of cellulase enzymes [55]. Up until the late 1960s, cellulase was studied in order to avoid degradation [56]. However, the combined pressures of municipal waste disposal and the need for alternate fuel sources due to the 1970s energy crisis [57] led researchers to investigate the possibility of producing fermentable glucose from cellulose. The immediate advantages of enzymatic hydrolysis of cellulose to glucose were that only glucose was produced [58] and that its mild hydrolysis conditions required no expensive construction materials. However, it was also immediately clear that enzymatic hydrolysis of native cellulosic feedstocks was slow with low yields [58]. These significant disadvantages prompted researchers to search for pretreatments to increase cellulose accessibility.

Han and Callihan reported one of the first examples of acidic pretreatment for application of a two-stage process to sugarcane bagasse [59]. In this system, bagasse was exposed to 10–50% H_2SO_4 for 15 minutes at 121 °C in the first stage, after which the reaction mixture was diluted to 0.5–2% H_2SO_4 and reheated to 121 °C for 15 minutes to 2 hours [59]. Han and Callihan recognized that this treatment improved performance of subsequent enzymatic hydrolysis but, because the digestibility of acid-treated bagasse by *Cellulomonas* and *Alcaligenes* was much lower than that of alkali-treated material, they concluded that acid pretreatment was not feasible [59]. Nesse *et al*. showed that pretreatment of fiber from feedlot manure using 0.01–3.5% peracetic acid for 1 hour at room temperature increased its digestibility [60]. The pretreatment used by Han and Callihan [59] was relatively severe, while that by Nesse *et al*. [60] was milder. Researchers at the Lawrence Berkeley Laboratory (LBL) found that batch pretreatment with 0.9 w/w% H_2SO_4 at 100 °C lasting up to 5.5 hours significantly improved yields from enzymatic hydrolysis of several agricultural residues including wheat straw, barley straw, rice straw, sorghum straw, and corn stover [61]. Combined glucose and xylose yields (defined as grams of monomer per gram of monomer equivalent in the raw biomass) from the enzymatic hydrolysis of pretreated material were 10–41% higher than yields from the enzymatic hydrolysis of raw biomass [61]. The LBL team also showed that very little acid was consumed during the pretreatment step for most of the tested substrates, which would be commercially beneficial.

Grethlein *et al*. [58], Knappert *et al*. [62], and Grethlein and Converse [63] used a continuous plug flow reactor to pretreat a wide variety of materials including newsprint [57], corn stover [62], oak [62], white pine [58], poplar [63], and mixed hardwood [58]. The concentration of H_2SO_4 was varied from 0.4–1.2% at 160–220 °C with reactor retention times of 6.6–13.2 seconds. Some of these pretreatment conditions were very effective at increasing susceptibility of native materials such as corn stover and oak to enzymatic

hydrolysis. It was found that different substrates required different pretreatments in order to achieve high enzymatic hydrolysis yields, with the improvements cautiously attributed to an increase in pore size and surface area. Many processes to increase the accessibility of cellulose to enzymes using acids were also patented; for example Foody patented a process to treat lignocellulosic material with 0.15–1 w/w% H_2SO_4 at 1.8–7.0 MPa [64].

6.3.3   Pretreatment for Improved Enzymatic Digestibility and Hemicellulose Sugar Recovery

The development of microorganisms capable of converting both pentoses and hexoses to ethanol over the past two decades has made it possible to derive value from all the sugars in hemicellulose and cellulose [65]. Consequently, the current paradigm for ethanol production from cellulosic biomass is to recover as much sugar as possible from cellulose and hemicellulose in the combined operations of pretreatment and enzymatic hydrolysis [66]. In line with this objective, successful pretreatments must not sacrifice sugars from hemicellulose, while modifying the remaining solids so that they are susceptible to enzymatic hydrolysis with high yields. It is also critical to limit formation of degradation products that inhibit enzymatic hydrolysis or fermentation [66]. Formation of degradation products also comes at the expense of fermentable sugars and thus ethanol. The goal to maximize sugar recovery is just as important for pretreatment applications to microbes now being developed to convert biomass to fuels other than ethanol such as hydrogen [67,68]. Despite the changing goals of pretreatment, many of the same chemicals such as SO_2 and H_2SO_4 are utilized because they lower pH effectively and are readily available at comparatively low prices. Additionally, SO_2 can be recovered and recycled following pretreatment; however, it is a more hazardous chemical to work with, and the recovery operations would increase capital and operating costs of a commercial operation. There is also limited literature on application of nitric, hydrochloric, or phosphoric acids to prepare biomass for biological conversion [66], and their higher costs could present economic challenges. Attempts have been made to use carbon dioxide as an acidifying agent [69–72] since it is produced during fermentation [73] and would be less corrosive than mineral acids [74]. However, yields from hydrolysis with carbon dioxide fall short of those from H_2SO_4 hydrolysis [74]. Furthermore, Jayawardhana and van Walsum [74] estimated that high-pressure carbon dioxide pretreatment reactors would be more expensive than for dilute acid pretreatment.

Since space considerations prevent inclusion of the complete body of research on low-pH pretreatments, the following sections provide a summary of thoroughly studied and commercially promising processes based on SO_2 and H_2SO_4 pretreatments. Representative works by leading investigators, both individual and institutional, are highlighted so that the reader can easily locate material for more in-depth information.

Pretreatment with Sulfur Dioxide

Sulfur dioxide has been used to treat a wide variety of biomass including softwoods such as Douglas fir [44], agricultural residues such as corn stover [75] and bagasse [18], and hardwoods such as poplar [75]. In most laboratory studies, biomass solids were impregnated with SO_2 at room temperature. After impregnation, the biomass was transferred to a pretreatment reactor, typically a steam explosion device, and injected with steam until the target reaction time was reached. At that point, a blow-down valve was opened to discharge the pretreated solid material and liquid hydrolysate to atmospheric pressure, cooling the materials almost instantly to 100 °C. A flow diagram of a sample experimental procedure and apparatus for SO_2 pretreatment was provided by Stenberg *et al.* [76]. Schell and co-workers provided a detailed process flow diagram of a potential commercial configuration for SO_2 pretreatment [77].

The length of impregnations varied. For example, Martín *et al.* [18] performed impregnations lasting 15–20 minutes while Boussaid *et al.* and Bura *et al.* [44,75] allowed impregnations to continue overnight.

Although most impregnations were performed without wetting the biomass, Öhgren *et al.* [17] and De Bari *et al.* [78] presteamed it prior to impregnation. However, as De Bari *et al.* [78] noted, when impregnated biomass is transferred from the adsorption vessel to the pretreatment reactor, some SO_2 is lost, making it difficult to compare results among researchers. Consequently, De Bari *et al.* [78] examined impregnation of aspen chips with SO_2 and the influence of moisture content using a custom-designed adsorption chamber. The chamber was placed on a high-resolution industrial weighing platform and, after chips were loaded, sufficient SO_2 was added to increase the weight by 4–5% of the aspen mass. The chamber pressure was monitored to estimate adsorption from the compressibility factor equation of state. After impregnation was complete, the biomass was removed from the reactor and the decrease in mass was monitored as excess SO_2 desorbed from the biomass. Once a constant mass was reached, the biomass was pretreated. De Bari *et al.* [78] found that, even after extended impregnation times, only 50% of the available gas was adsorbed with most of it being adsorbed during the first 15 minutes. It was also found that approximately half of the adsorbed gas was lost during outgassing, leaving an adsorbed concentration of 0.6–0.9 SO_2 w/w% raw, dry biomass. Increasing the biomass moisture content slightly increased the final amount of SO_2 adsorbed. This study [78] aptly illustrated the challenges of controlling SO_2 impregnation and accurately determining the effective SO_2 concentration during pretreatment.

Two-stage pretreatment systems have been used in an attempt to increase total sugar recovery [79]. The first stage was optimized for recovery of hemicellulosic sugars, while the second step was optimized for enzymatic digestibility of biomass. Although it was possible to increase final ethanol yields and decrease enzyme usage through such two-stage pretreatments, it is unclear whether these improvements justify the additional costs and technical challenges.

Table 6.2 reveals that although SO_2 has been applied to a diverse range of biomass types, the pretreatment conditions were quite similar: SO_2 concentration ranged from 1.1 to 4.5%, temperatures between 170 and 220 °C, and times from 2 to 10 minutes. However, as De Bari *et al.* [78] demonstrated, the concentration of SO_2 used for impregnation did not accurately reflect the amount of SO_2 adsorbed.

Pretreatment with SO_2 results in the release of hemicellulose sugars and some lignin as well as degradation products at high severities. There are conflicting reports as to the effects of steam explosion with SO_2 on the degree of polymerization of the sugar products. When Boussaid *et al.* [44] and Söderström *et al.* [79] pretreated softwoods such as Douglas fir and *Picea abies* with SO_2, mannose (the primary hemicellulose

Table 6.2 *Selected conditions for pretreatment with sulfur dioxide prior to biological conversion. Yield is defined as gram carbohydrate equivalent in the liquid hydrolysate following pretreatment per gram of carbohydrate equivalent in the raw biomass.*

Substrate (Author)	SO$_2$ Concentration (%)	Temperature (°C)	Time (min)	Yield (w/w%)	Concentration (g/L)
Douglas fir (Boussaid *et al.* [44])	2.38–4.5	175–215	2.38–7.5	Mannose yield: 22–49%	
Corn stover, poplar (Bura *et al.* [75])	3	170–215	5–9		11.2–23.7 g xylose/L hydrolysate
Sugarcane bagasse (Martín *et al.* [18])	1.1	205	10	Xylan yield: 27%	
Corn stover (Öhgren *et al.* [17])	3	200	5		35.8 g xylose/L hydrolysate
Picea abies (Söderström *et al.* [79])	3	180–220	2–10	2-stage mannan yield: 91–96%	

sugar in softwood) was recovered as a monomer. In contrast, Bura *et al.* [75] found that SO_2 pretreatment of corn stover and poplar produced a lot of oligomers from hemicellulose, and especially xylooligomers. These differences may be due to differences in biomass or in pretreatment conditions. Biomass differences seem the more likely cause as the pretreatment conditions used by Bura *et al.* [75] overlap those used by Boussaid *et al.* [44] and Söderström *et al.* [79].

Several studies observed that little lignin was removed by SO_2 pretreatment [44,75,78]. De Bari *et al.* [78] found that the amount of lignin increased slightly for high-severity pretreatments and attributed this to formation of Klason-lignin-like by-products. A number of phenolic compounds such as p-coumaric acid, ferulic acid, and 4-hydroxybenzaldehyde were also released by SO_2 pretreatment [18].

As the severity of pretreatment was increased, sugars were degraded to 5-hydroxymethylfurfural (5-HMF-), furfural, and other non-sugar compounds [18,44,75,78,79]. Interestingly, Martín *et al.* [18] found that the concentrations of furfural, 5-HMF, levulinic acid, and formic acid in the hydrolysate from SO_2-catalyzed steam explosion were similar to concentrations found in the hydrolysate from uncatalyzed steam explosion, and the xylose yields from SO_2 pretreatment were only slightly higher than from steam explosion. This outcome may be because the effective SO_2 concentration decreased as biomass was transferred to the reactor or because SO_2 does not significantly accelerate degradation reactions.

Pretreatment with Sulfuric Acid

Dilute sulfuric acid has been by far the most common acid catalyst used for biomass pretreatment prior to biological conversion. Like SO_2, it has also been used to pretreat a wide variety of biomass types. Biomass is frequently soaked in dilute acid prior to pretreatment, and the reactors used for pretreatment with H_2SO_4 are almost as diverse as the types of biomass tested. Various possible commercial processes based on dilute sulfuric acid pretreatment have been designed over the years, with a recent design by Humbird *et al.* being one example [80]. In the case of biological conversion of the cellulose in biomass to glucose, a key research goal has been to reduce the amount of H_2SO_4 used for pretreatment.

Batch reactors are commonly applied for dilute acid pretreatments, and both unstirred reactors and stirred reactors have been used. For example, Lloyd and Wyman employed both reactor types to pretreat corn stover [26]. Small tube reactors typically have an inner diameter of about 10.8 mm to reduce temperature non-uniformity [81,82] with a length of about 100 mm, allowing reasonable quantities to be processed. A larger stirred reactor with a volume of 1.0 L and an 88.9 mm helical-impeller-provided agitation was also used by Lloyd and Wyman [26]. The reactors were loaded with a corn stover slurry at 5% solids with 0.22–0.98% H_2SO_4 by weight in the water. Pretreatment temperatures varied from 140 to 180 °C for times up to 80 minutes. After pretreatment, the solids were subjected to enzymatic hydrolysis with cellulase supplemented with beta-glucosidase. Lloyd and Wyman [26] observed significant production of xylooligomers, especially for short pretreatment times, but the fraction of xylooligomers relative to total xylose release decreased as the concentration of acid increased. This paper illustrated the classic conundrum of dilute acid pretreatment: how to maximize sugar yields from enzymatic hydrolysis favored by long reaction times, while minimizing degradation reactions during pretreatment that occur at long reaction times. In this application, Lloyd and Wyman [26] showed that the maximum yields of glucose, xylose, and glucose plus xylose together in pretreatment and enzymatic hydrolysis did not occur for the same pretreatment conditions. When selecting pretreatment conditions, it is therefore important to maximize release of all relevant sugars from pretreatment, enzymatic hydrolysis, and all subsequent operations.

Dilute sulfuric acid has also been used in steam explosion systems. Sassner *et al.* [83] used such reactors to pretreat wood chips from a *Salix* hybrid that were presoaked in 0.25–0.5% H_2SO_4 for at least 90 minutes. The solids were recovered by filtration and then transferred to a 10 L steam

explosion unit, with pretreatment temperatures ranging from 180 to 210 °C and times from 4 to 12 minutes. The liquids and solids from pretreatment were subjected to fermentation and enzymatic hydrolysis, respectively. Additionally, simultaneous saccharification and fermentation (SSF) of various dilutions of the pretreated *Salix* hydrolysate slurry was performed. During SSF, biomass was combined with enzymes and a fermentative microbe, such as yeast, so that monomers produced by enzymatic saccharification were fermented to ethanol soon after release to reduce inhibition of the enzymes by sugars. One unique feature of this work was that collection and analysis of the exhaust gases and hydrolysate from pretreatment revealed high concentrations of furfural and acetic acid. Sassner *et al.* found that xylose degradation decreased when the initial moisture content of the chips was increased [83]. A high initial moisture content increased steam condensation and appeared to improve fermentations by diluting potential inhibitors [83]. The pretreated solids were easily digested during enzymatic hydrolysis despite retaining 74–95% of the lignin in the raw biomass [83].

Cahela *et al.* [84] pretreated southern red oak in a percolation reactor with 0.2% H_2SO_4. The reactor had an inner diameter of 25.4 mm and a length of 627 mm and could be loaded with 120–140 g of red oak sawdust. As described in greater detail in Section Xylose Production, they also developed a model of hemicellulose hydrolysis for a packed bed that accounted for diffusion of products from the interior of the biomass particle to the bulk liquid. In general, their experimental results and model predictions agreed within 10%, with discrepancies primarily attributed to difficulties in determining the true H_2SO_4 concentration due to the buffering effects of ash in the wood.

Mok *et al.*'s [85] work provided a second example of percolation pretreatment with H_2SO_4; however, in this work the objective was glucose recovery. The reactor consisted of two chambers: the primary chamber with a diameter of 4.6 mm and a length of 76 mm used to hold the solid substrate, and a secondary chamber with variable volume to study the influence of liquid phase reactions. Whatman no. 1 and no. 4 filter papers were used as substrates. The flow rate of 0.05% H_2SO_4 was varied from 2 to 4 mL/min, and the pretreatments lasted from 0 to 60 minutes at 190–225 °C. Although the classic Saeman model of cellulose hydrolysis [86] (see Section 6.1.1) predicted that decreasing the volume of the secondary reaction chamber would increase the yield of glucose by limiting degradation reactions, Mok *et al.* found that the glucose yield decreased; this led them to propose that cellulose hydrolysis first generates oligomers that are further hydrolyzed to glucose [85]. Mok *et al.* also suggested that the increase in glucose yield with increasing flow rate was due to the removal of soluble products prior to degradation [85].

As with the use of SO_2, the conundrum of minimizing xylose degradation during pretreatment while achieving high digestibility of cellulose in the pretreated solids can be addressed by two-stage pretreatments with dilute sulfuric acid. Nguyen *et al.* [87] tested one such configuration using a mixture of white fir (*Abies concolor*) and Ponderosa pine (*Pinus ponderosa*). Softwood chips were soaked in 0.6–2.4% H_2SO_4 for 4 hours at 60 °C and then added to a 4 L steam explosion reactor. During the first pretreatment, the temperature was varied from 180 to 215 °C for 1.6–4 minutes, giving a combined severity for the first stage pretreatment ranging from 2.18 to 3.26. At the completion of this time, the solids were washed to remove solubilized hemicellulose sugars and then soaked in 2.5% H_2SO_4 for 3 hours at ambient temperature before being treated at 210 °C for 1.6–2 minutes. The solids from this two-stage approach were employed in both enzymatic hydrolysis and SSF. The total sugar yields from two-stage pretreatment followed by enzymatic hydrolysis was slightly higher than the total sugar yields from single-stage pretreatment followed by enzymatic hydrolysis. In addition, two-stage pretreatment could potentially reduce enzyme usage as the cellulose content in the solids from the second pretreatment stage was lower than for one-stage pretreatment. However, as with the two-stage SO_2 pretreatment, it is unclear that the performance gains from two-stage pretreatment justify the additional costs.

Pretreatment conditions reviewed in this section are summarized in Table 6.3.

Table 6.3   *Selected conditions for pretreatment with sulfuric acid prior to biological conversion. Yield is defined as gram carbohydrate equivalent in the liquid hydrolysate following pretreatment per gram of carbohydrate equivalent in the raw biomass.*

Substrate (Author)	Concentration	Temperature (°C)	Time (min)	Yields
Southern red oak (Cahela *et al.* [84])	0.037–0.056 w/v%	140–160	*c.* 14–115	Xylan yield: *c.* 8.8–88%
Whatman paper no. 1 and 42 (Mok *et al.* [85])	5 mM	190–225	0–60	Glucose yield: *c.* 35–85%
Corn stover (Lloyd and Wyman [26])	0.22–0.98%	140–200	0–80	Maximum xylose yields of 71–85%
White fir and Ponderosa pine (Nguyen *et al.* [87])	0.6–2.5%	180–215	1.7–4	2 stage mannose+ galactose+ xylose+ arabinose yield: 84%
Salix hybrid (Sassner *et al.* [83])	0.25–0.5 w/w%	180–210	4–12	Xylose yield: *c.* 55–75%

6.4 Low-pH Hydrolysis of Cellulose and Hemicellulose

There has been growing interest in producing "drop-in" hydrocarbon fuels from biomass, that is to say, hydrocarbons that can be easily integrated with today's motor vehicles and airplanes. Additionally, since many of today's chemical feedstocks are derived from petroleum, there is a need to generate alternative chemical feedstocks from biomass. Although pretreatment traditionally refers to the preparation of biomass for biological conversion, researchers are now also applying low-pH reactions to produce reactive intermediates for catalytic chemical conversion to fuels and chemicals. In a sense, these reactions are also "pretreatments" and certainly share similar features to historical pretreatment technologies. However, the pretreatment conditions to support catalytic conversion tend to be much more varied due to the wider range of downstream processing objectives.

6.4.1 Furfural

One of the oldest examples of industrial chemical production from biomass is furfural manufacture from the xylan and arabinan in hemicellulose. Furfural is currently used for such applications as resins, linking foundry sand, lubrication oil extraction, and nematicides [88], but could be used to produce a wide variety of other chemicals. The first industrial production of furfural used oat hulls as a feedstock to take advantage of its high xylan content [88], and major industrial feedstocks today are corn cobs and bagasse [24].

Furfural can be produced by a one- or two-stage process [89]. In the one-stage process, biomass is combined with approximately 3% H_2SO_4 by weight in a slurry [90], and steam is introduced to bring the reactor to the desired temperature. The hemicellulose is hydrolyzed to xylose and arabinose, which in turn are dehydrated to furfural [91]. Furfural is continuously removed from the reactor in the vapor phase to reduce decomposition and recondensation reactions [89]. The reactor is typically held at 170–185 °C for 3 hours, and the process results in furfural yields of approximately 40–50% of the theoretical maximum. One of the challenges in this process is the rapid recovery of furfural, but the efficiency of recovery by steam injection is limited due to the boiling point elevation in the reactor as biomass components are solubilized. The two-stage process attempts to separate hemicellulose hydrolysis and xylose cyclodehydration reactions, with hemicellulose hydrolysis conducted at milder conditions to generate a pentose-rich liquid stream for dehydration. By separating the two reactions, it is also possible to produce a cellulose-lignin substrate that can also be converted to chemicals or fuel. A review by Mamman *et al.* [90] identified a number pretreatments resulting in high xylose yields, with some of these summarized in Table 6.4.

Table 6.4   *Selected pretreatment conditions for high xylose yields in support of furfural production [90].*

Biomass	w/w% H_2SO_4	Temperature (°C)	Time (minutes)
Oil palm empty fruit bunch	4	115	60
Corn fiber	0.75	121	30
Switchgrass	0.5	140–160	10–60

A new field of study in the production of furfural is the use of chloride salts to increase the xylose production rate [92]. Marcotullio and De Jong [92] showed that furfural yields and selectivity increased when chloride salts such as NaCl and $FeCl_3 \cdot 6H_2O$ were added to the cyclodehydration of xylose with dilute hydrochloric acid; the addition of salts increased the reaction rate even for low acid concentrations. Of the salts tested, $FeCl_3 \cdot 6H_2O$ seemed particularly promising due to a dramatic increase in xylose reaction rates. Although details of the mechanism for the conversion of xylose to furfural are unresolved, Marcotullio and De Jong [92] hypothesized that chloride ions promote formation of 1,2-enediol that may be an important intermediate to furfural production.

6.4.2   Levulinic Acid

Levulinic acid is a chemical that could be made from the cellulose fraction of biomass for use as a feedstock to make diesel and gasoline additives. Rackemann and Doherty recently provided a thorough review of the uses and production of levulinic acid from biomass [93]. The Biofine process was developed to produce levulinic acid from a cellulosic biomass feed [8], and a number of different substrates were tested including waste paper, waste wood, and agricultural residues. In this case, solids were combined with 2–5% H_2SO_4 at ambient temperature and then pumped into a short continuous plug flow reactor, held at 215 °C and 3.1 MPa(g) with a residence time of 15 seconds, to release glucose. The slurry was then pumped to a continuous stirred tank reactor at 193 °C and 1.4 MPa(g) with a residence time of 12 minutes. Slow conversion of sugars to levulinic acid occurred during this stage; the process generated approximately 0.5 kg levulinic acid/kg cellulose. Furfural and formic acid were also produced.

6.4.3   Drop-in Hydrocarbons

An emerging processing paradigm is to pretreat biomass in order to release reactive intermediates that can be catalytically converted to drop-in hydrocarbons. The objectives of pretreatment in support of these catalytic processes are to maximize intermediate yields and avoid use or generation of catalyst poisons [94]. One example of pretreatment for this type of process was presented by Li *et al.* [95] in which maple wood was pretreated in 0.5% H_2SO_4 in a steam gun at temperatures of 160–180 °C for 10–30 minutes [95]. They then subjected the resulting carbohydrate-rich liquid stream to low-temperature hydrogenation to produce sorbitol and xylitol, which were then converted to gasoline range hydrocarbons. Both of these steps used heterogeneous catalysts. The cellulose- and lignin-rich solids from pretreatment could then be used in other processes such as ethanol production [95].

Because mineral acids could deactivate downstream metallic catalysts [95], two possible solutions have been employed to address this challenge. In the first, the pretreatment liquor is neutralized prior to catalysis but, as discussed in Section 6.1, this approach is not ideal. The second alternative is to pretreat biomass with an organic acid such as oxalic acid ($C_2H_2O_4$) [94]. For example, Zhang *et al.* [94] applied pretreatments lasting 5–60 minutes at 160 °C using H_2SO_4, HCl, and $C_2H_2O_4$ at concentrations of 0.5–2%, and found that $C_2H_2O_4$ pretreatments resulted in slightly higher carbon recoveries than pretreatment with mineral acids

[94,95]. In general, the highest xylose monomer recovery was achieved at low acid concentrations. For example, Li *et al.* [95] reached their maximum xylose recovery using 0.5% $C_2H_2O_4$ at 180 °C for 10 minutes. At 160 °C, Zhang and Wyman's maximum total xylose recoveries, defined as xylose equivalent of monomers and oligomers in the liquid phase as a percentage of xylose equivalents available in the raw biomass, were 84.4%, 73.8%, and 87.5% with 0.5% H_2SO_4 for 30 min, 0.5% HCl for 10 min, and 0.5% $C_2H_2O_4$ for 30 min, respectively [94]. The higher cost of $C_2H_2O_4$ relative to mineral acids could however limit its use as a catalyst, but no process designs have yet been applied to estimate the tradeoffs for use of oxalic vs. mineral acids. Furthermore, the impact of pretreatment acid type on downstream operations has not been fully investigated.

Recycling $C_2H_2O_4$ will be likely key to its use on a commercial scale. Vom Stein *et al.* fractionated beechwood using a biphasic system of an aqueous phase containing wood and oxalic acid in contact with 2-methyltetrahydrofuran (2-MTHF) at temperatures of 125–150 °C [96]. Little $C_2H_2O_4$ reacted at temperatures between 125 °C and 140 °C, but only 70% of $C_2H_2O_4$ was recovered after reaction at 150 °C, suggesting side reactions may be significant at this temperature. They also found that $C_2H_2O_4$ could be recovered by crystallization after reaction and re-used [96]. However, further work is required to fully evaluate the advantages and disadvantages of using $C_2H_2O_4$ with and without recycle relative to mineral acids.

Another biomass conversion system based on dilute acid pretreatment is the production of gasoline-compatible hydrocarbons via simultaneous hydrolysis and hydrogenation. In this configuration, a metallic catalyst in an acidic aqueous solution with a hydrogen headspace promotes biomass reactions. The reactor is heated to initiate biomass hydrolysis to monomeric sugars, which are then immediately converted to sugar alcohols such as sorbitol over the metallic catalyst for conversion into hydrocarbons in downstream operations. In a study by Robinson *et al.* [97], idealized substrates and native biomasses such as switchgrass were treated in stirred batch reactors with ruthenium catalyst on a carbon support [97]. Solutions with 0.7% H_2SO_4 and 0.35–1.5% H_3PO_4 were tested at temperatures in the range 160–193 °C over a time period of 3–17 hours. A more recent example of simultaneous hydrolysis and hydrogenation was reported by Palkovits *et al.* [98] in which they tested idealized substrates such as α-cellulose and native spruce. The catalysts Pt-C, Pd-C, and Ru-C were applied in 0.5–2.5% H_3PO_4 and H_2SO_4 at 160 °C for 1–5 hours to produce 5- and 6-carbon alcohols as well as glucose and xylose. Higher conversion of cellulose was obtained using H_2SO_4 compared to phosphoric acid, likely due to the higher pKa value of H_2SO_4 [98]. Interestingly, this study showed that although overall conversion using the Ru-C catalyst was low in comparison to Pt and Pd catalysts, the Ru-C catalyst gave higher yields of desired products. Additionally, production of xylose and glucose were greater in the presence of the heterogeneous catalysts than traditional acid hydrolysis.

6.5   Models of Low-pH Biomass Reactions

For almost as long as biomass hydrolysis has been studied, there have been efforts to develop kinetic models of the system. Such models have been difficult to develop due to the complexity of the system (the solid–liquid interactions of the biomass and the aqueous phase; the challenges of determining the effective acid concentration during reaction; interactions among cellulose, hemicellulose, and lignin) and the complexity of the composition of these fractions. In addition to the complex reaction scheme, there are also the challenges in assessing and modeling mass and heat transfer within the reactor and biomass. Finally, the diversity and range of biomass and associated chemical bonds within hemicellulose and with lignin likely limit the extent to which models can be accurately applied. However, it is vital to address these challenges because of the utility of kinetic models in research and industrial production. Models provide a framework to test hypotheses in an efficient and targeted manner. Reliable kinetic models are also vital to the scaling-up of pretreatment from the lab to commercial production. Finally, models assist in determining optimum biomass feedstock and processing configurations.

6.5.1   Cellulose Hydrolysis

Glucose Production

As the early goal of low-pH biomass reactions was cellulose hydrolysis to glucose, much of the kinetic modeling literature of that time focused on acid-catalyzed hydrolysis of cellulose via the proton-catalyzed cleavage of the glycosidic bond [99]. One of the first models was based on the following series of first-order pseudo-homogeneous reactions by Saeman [86]:

$$\text{cellulose} \xrightarrow{\quad k_1 \quad} \text{glucose} \xrightarrow{\quad k_2 \quad} 5-\text{HMF} \tag{6.2}$$

where

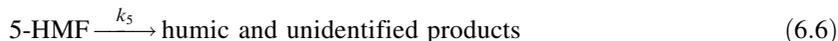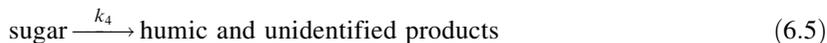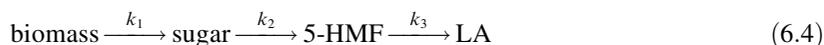$$k_i = H_i C_a^M \exp\left(\frac{-\Delta H_{a,i}}{RT}\right) \tag{6.3}$$

where k_i is the reaction rate constant (min^{-1}) for reaction i, H_i is a constant, C_a is the concentration of H_2SO_4 (%) and M is the reaction order, $\Delta H_{a,i}$ is the activation energy, R is the universal gas constant, and T is the absolute temperature. This model has been the basis of almost every cellulose and hemicellulose hydrolysis model since. Saeman [86] applied his model to a variety of substrates including red oak, Douglas fir, hard maple, and aspen and found that hydrolysis rates did not differ by more than 20%. These differences could be partially explained by differences in buffering capacity of the wood: substrates with the lowest ash content were found to have the highest hydrolysis rates. Saeman [86] also studied hydrolysis of Douglas fir at a variety of temperatures and acid concentrations and found that the activation energy was independent of acid concentration, while the rate constant increased by 153% for a 100% increase in acid concentration. Definition of acid concentration C_a has been challenging in part due to the neutralizing capacity of biomass. In the past, C_a has been expressed in terms of mass, molarity, and pH at room temperature [100], and variations in definition may help explain the wide variation in kinetic rate constants for hydrolysis. Lloyd and Wyman [100] demonstrated that the neutralizing capacity of biomass and the temperature have a significant influence on the pH of a system, a fact well worth considering in future modeling.

One of the first modifications to Saeman's model was adjustment of his assumption that the initial glucose concentration was zero. In particular, amorphous cellulose hydrolyzed quickly enough to be included as an initial glucose concentration [101]. Most subsequent modifications have added decomposition reactions and parallel reactions. For example, Conner *et al.* [102] added reversible formation of levoglucosan from glucose and disaccharides, and Bouchard *et al.* [103] found evidence for a parallel pathway that modifies cellulose to a structure that cannot be hydrolyzed to glucose. Abatzoglou *et al.* [104] added formation of glucoligomer intermediates as a sequential step to Saeman's model. Mok *et al.* [85] searched for additional evidence of these phenomena and, after eliminating the possibilities that chemical alteration of residual solid cellulose or glucose degradation reactions were responsible for limiting glucose yield, they concluded that unknown products that could not be hydrolyzed to glucose were produced during pretreatment.

5-HMF and Levulinic Acid Production

Levulinic acid is produced from the dehydration of hexose sugars. Production from biomass is based on cellulose first being hydrolyzed to glucose, which then undergoes dehydration to 5-HMF and its reaction to levulinic acid. However, many significant side reactions also occur, lowering the final yield of levulinic acid. Several models have been developed to describe the formation of levulinic acid from glucose [105–107]. Chang *et al.* modeled glucose conversion to 5-HMF and on to levulinic acid

(LA) as a series of first-order unimolecular reactions and incorporated parallel reactions for conversion of glucose and 5-HMF to humic solids [108]:

$$\text{biomass} \xrightarrow{\ k_1\ } \text{sugar} \xrightarrow{\ k_2\ } \text{5-HMF} \xrightarrow{\ k_3\ } \text{LA} \tag{6.4}$$

$$\text{sugar} \xrightarrow{\ k_4\ } \text{humic and unidentified products} \tag{6.5}$$

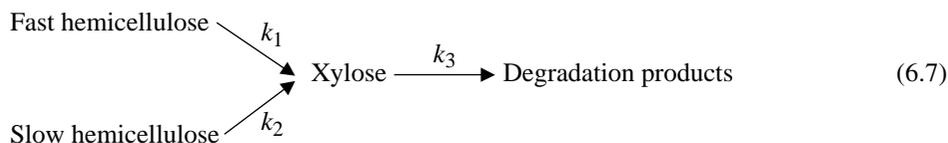$$\text{5-HMF} \xrightarrow{\ k_5\ } \text{humic and unidentified products} \tag{6.6}$$

Girisuta *et al.* applied a similar mechanism [106]. Assary *et al.* developed quantum mechanics models for glucose conversion to levulinic acid [107]. They also showed that the first two steps, tautomerization of α-D-glucose to β-D-fructose and dehydration of β-D-fructose to an intermediate, were endothermic and indicated that initial dehydration of β-D-fructose was the rate-limiting step [107]. After developing models for glucose conversion to levulinic acid, Girisuta *et al.* developed a kinetic model for conversion of purified, crystalline cellulose to levulinic acid [109]. This model was then adapted to conversion of biomass such as water hyacinth leaves by including conversion of galactose released from hemicellulose and adding a correction factor to account for differences in cellulose properties [110]. The correction factor for conversion of hexoses to levulinic acid was found to be less than 1, indicating that the conversion of cellulose in biomass is lower than that of pure cellulose. It was also shown that the correction factor for humin formation from hyacinth leaves was approximately 2, indicating that the rate of humin production from hyacinth leaves was greater than the rate of production from pure cellulose. Chang *et al.* developed a model for levulinic acid production from wheat straw based on first-order unimolecular reactions with a power law dependence for acid concentration [108]. It was found that the reaction order of the acid concentration ranged from 0.620 to 1.434.

6.5.2   Hemicellulose Hydrolysis

Xylose Production

In general, hemicellulose hydrolysis models are less well-developed than those for cellulose; hemicellulose hydrolysis has been of interest for a shorter period of time and the composition and structure of hemicellulose is more complex than that of cellulose. Although many hemicellulose hydrolysis models were simply adaptations of Saeman's approach to describe cellulose deconstruction, Kobayashi and Sakai [111] assumed that xylose was released from fast and slow reacting fractions, as shown in Equation (6.7):

$$
\begin{array}{l}
\text{Fast hemicellulose} \searrow {\scriptstyle k_1} \\
\phantom{\text{Fast hemicell}} \text{Xylose} \xrightarrow{\ k_3\ } \text{Degradation products} \\
\text{Slow hemicellulose} \nearrow {\scriptstyle k_2}
\end{array} \tag{6.7}
$$

However, each reaction was still modeled using the first-order pseudo-homogeneous system employed by Saeman. Jacobsen and Wyman [101] reported seven examples of this model. Hemicellulose hydrolysis models have also incorporated production of xylooligomer intermediates [101], and parallel reactions of other hemicellulose constituents such as acetyl groups have also been included [16].

The combined severity factor, Equation (6.1), was an important development by Abatzoglou *et al.* [2] and Chum *et al.* [3]. This parameter facilitates comparison of the combined effects of temperature, time, and acid concentration and tradeoffs among them with reaction conditions. It is important to acknowledge

that although the combined severity parameter can be useful in comparing datasets collected at different temperatures and acid concentrations, it cannot reliably predict specific performance as Lloyd and Wyman [26] demonstrated with their study of dilute acid pretreatment of corn stover.

Several studies have attempted to include the effects of diffusion in biomass particles on hemicellulose hydrolysis [42,112]. Tillman and co-workers experimentally determined the diffusivity of H_2SO_4 in the longitudinal and radial directions of hardwood and showed that the diffusivity in the radial direction was much larger [112]. The diffusivity coefficient was then combined with a biphasic hemicellulose hydrolysis model to predict the spatial dependence of xylose production within hardwood particles of increasing size. The results showed that, as the reaction temperature increased, xylose yields dropped due to incomplete acid diffusion [112]. Kim and Lee expanded this work to study the transport properties of H_2SO_4 in sugar cane bagasse, corn stover, rice straw, and yellow poplar [42]. Their results showed that diffusivities in agricultural residues were significantly larger than in yellow poplar and that the diffusion of acid into biomass could significantly impact hemicellulose hydrolysis results depending on particle size, reaction temperature, and reaction time.

As stated in Section 6.3.3, Cahela *et al.* [84] developed a model to account for the diffusion of reaction products out of biomass particles. Hemicellulose was assumed to hydrolyze to xylose and xylooligomers, which then degraded to furfural via first-order homogeneous reactions. They refined their model by differentiating between the xylose concentration within the pores of the biomass particles and the xylose concentration in the bulk liquid, and the resulting coupled differential equations were solved as the reaction time became large. From this model, they predicted the maximum xylose yields and associated concentrations as well as operating conditions required to achieve these results. They also found that intraparticle diffusion of xylose oligomers could be important if the longitudinal chip dimension was greater than 4.2 mm. Because this represents a relatively small particle, mass transfer effects could well be of consequence in industrial operations with large biomass particles. Hosseini and Shah [113] took this analysis even further with a more detailed kinetic mass-transfer model that attempted to account for differences in xylooligomer reactivity by assuming that bond breakage is a function of position in the xylooligomer chain. Predictions from this approach strongly correlated with experimental data for hydrolysis of xylooligomers with a degree of polymerization less than or equal to five. Consideration of diffusion of individual oligomer products out of biomass particles showed that the concentrations of xylooligomers within the chip predicted by the model were very sensitive to the assumed value of the diffusion coefficient. This work, as well as others, demonstrated the importance of considering xylooligomer intermediates in kinetic modeling.

The effect of temperature gradients within biomass particles or reactors has also been incorporated into some models. Abasaeed *et al.* [114] and Abasaeed and Mansour [115] provided two examples of the effects of temperature gradients within biomass particles on the results of cellulose hydrolysis. The former applied a Saeman-type model to the hydrolysis of cellulose in southern red oak, determined the thermal diffusivities of southern red oak chips saturated with water, and then simultaneously solved the mass and energy balances of a wood chip. Their models showed that increasing the particle size reduced the maximum achievable glucose yield relative to that predicted based on assumed isothermal conditions, and that it took longer to reach this maximum. Increasing temperature and acid concentration exacerbated the effects of non-isothermal operation. Abasaeed and Mansour [115] modeled the effects of non-isothermal conditions in wood chips using three cellulose hydrolysis models from the literature and came to similar conclusions.

Stuhler and Wyman [82] examined the effects of temperature gradients within tubular batch reactors and applied a parameter β to represent the rate of xylan hydrolysis relative to the rate of heat conduction in the radial direction in a batch tubular reactor. They found that, when a radial temperature gradient developed within the reactor, there was a substantial reduction in xylan hydrolysis and that the erroneous assumption of isothermal conditions introduced significant errors in predicting xylan conversion. From these studies, it is clear that thermal gradients within biomass particles and reactors can have considerable impact on

product yields. Heat transfer therefore must be carefully considered for experimentation, modeling, and commercialization.
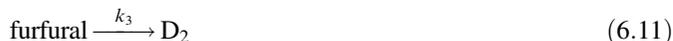
Furfural Production

In the previous section, researchers were primarily focused on models that could be used to optimize xylose recovery. In this section, however, the target is primarily to maximize furfural production. However, cyclo-dehydration of xylose to furfural is accompanied by numerous side reactions that make it complex to model. As a result, greater emphasis on furfural consuming reactions is needed to predict furfural concentrations.

The simplest kinetic models of furfural destruction assumed that furfural degrades to decomposition products according to a pseudounimolecular reaction [116,117]:

$$F \rightarrow D \tag{6.8}$$

In these studies, the rate of disappearance of furfural was found to be first order with respect to furfural concentration. Williams and Dunlop [116] applied a rate law for furfural disappearance at 150–210 °C in 0.1 M H_2SO_4 to show that the rate of furfural disappearance at 160 °C in 0.05 M HCl and 0.1 M H_2SO_4 were very close, leading them to postulate that the rate of destruction of furfural was first order with respect to hydrogen ion concentration. However, because the hydrogen ion concentration was high, it remained essentially constant during a run.

Weingarten *et al.* [25] developed a slightly more detailed reaction scheme for furfural production from xylose:

$$xylose \xrightarrow{k_1} furfural + 3H_2O \tag{6.9}$$

$$xylose + furfural \xrightarrow{k_2} D_1 \tag{6.10}$$

$$furfural \xrightarrow{k_3} D_2 \tag{6.11}$$

Each reaction was modeled as first order with respect to the reactants and hydrogen ion concentration. One of the most detailed models of furfural production from xylose was developed by Antal *et al.* who tracked production and destruction of 11 different compounds [23]. Through experimentation and modeling, they determined the open-chain xylose isomer was rapidly converted to undesirable products such as formic acid while the xylopyranose ring underwent dehydration to furfural. Unfortunately xylopyranose also reacted to undesirable products.

Nimlos *et al.* [118] subsequently developed quantum mechanics models of the energetics of these reactions to estimate transition states and energy barriers associated with three different reaction schemes for xylose decomposition to furfural. Based on energy barriers, Nimlos *et al.* [118] concluded that the model of Antal *et al.* [23] for the protonation of xylopyranose followed by dehydration to furfural was the most likely furfural production mechanism.

6.5.3   Summary of Kinetic Models

Given the highly empirical nature of the kinetic models that have been developed to date, anyone planning to apply kinetic models to biomass deconstruction with dilute acids would be well advised to employ a model developed for similar biomass and hydrolysis conditions. In this regard, Table 6.5 summarizes some of the biomass types, hydrolysis conditions, and general model types that have been applied. However, because an exhaustive table is beyond the scope of this chapter, it should serve merely as a starting point for the interested reader. In addition, in light of their empirical nature, it is vital to confirm models with data collected at relevant conditions to validate their accuracy.

Table 6.5   *Kinetic models of acid hydrolysis by biomass type and hydrolysis conditions.*

Source	Biomass	Temperature (°C)	Acidifying agent	Model description
Abasaeed *et al.* [114]	Southern red oak	198–215	1–3% H_2SO_4	Sequential hydrolysis of cellulose with intraparticle heat transfer
Abasaeed and Mansour [115]	Cellulose	T=180	0.4–2% H_2SO_4	Sequential hydrolysis of cellulose with intraparticle heat transfer
Abatzoglou *et al.* [104]	Cellulose	200–240	0.2–1.0 w/w% H_2SO_4	Sequential hydrolysis of cellulose with oligomer intermediates
Abatzoglou *et al.* [2]	Corn stalk, alfa, *Populus tremuloides, Betula papyrifera*	100–240	0–1.8% H_2SO_4	Severity parameter to predict xylan conversion
Aguilar *et al.* [16]	Sugar cane bagasse	100–128	2–6% H_2SO_4	Sequential hydrolysis of glucan and xylan; models for acetic acid and furfural
Antal *et al.* [23]	Xylose	250	0–20 mM H_2SO_4	Detailed model of xylose dehydration
Assary *et al.* [107]	Glucose			Quantum mechanics modeling of glucose decomposition to levulinic acid
Brennan and Wyman [119]	Corn stover	180	0.5–1.0 w/w% H_2SO_4	Mass transfer only models
Cahela *et al.* [84]	Southern red oak	140–160	0.037–0.056 w/v% H_2SO_4	Sequential hydrolysis of xylan with mass transfer effects
Canettieri *et al.* [22]	*Eucalyptus grandis*	130–160	0.65% H_2SO_4	Biphasic, sequential hydrolysis of xylan
Carrasco and Roy [120]	Corn stover, poplar, wheat straw, bagasse, paper birch	80–260	0.5–4 w/w% H_2SO_4	Biphasic, sequential hydrolysis of xylan with oligomer intermediates
Chang *et al.* [105]	Glucose	170–210	1–5% H_2SO_4	Sequential destruction of glucose to levulinic acid
Chang *et al.* [108]	Wheat straw	190–230	1–5 w/w% H_2SO_4	Sequential destruction of cellulose to levulinic acid with parallel degradation path
Chum *et al.* [3]	*Populus tremuloides*	125–145	0.2–1.7 w/w% SO_2	Severity parameter to predict xylan conversion
Converse *et al.* [121]	90% birch, 10% maple	160–265	0.2–2.4 w/w% H_2SO_4	Sequential hydrolysis of glucan and xylan
Esteghlalian *et al.* [43]	Corn stover, poplar, switchgrass	140–180	0.6–1.2 w/w% H_2SO_4	Biphasic, sequential hydrolysis of xylan
Girisuta *et al.* [106]	Glucose	140–200	0.05–1 M H_2SO_4	Sequential decomposition of glucose to levulinic acid
Girisuta *et al.* [109]	Microcrysalline cellulose	150–200	0.05–1 M H_2SO_4	Sequential decomposition of cellulose to levulinic acid
Girisuta *et al.* [110]	Water hyacinth	150–175	0.1–1 M H_2SO_4	Sequential decomposition of cellulose to levulinic acid; correction factor for biomass matrix
Hosseini and Shah [113]	Hemicellulose	T=160C	H_2SO_4	Xylooligomer depolymerization
Jacobsen and Wyman [101]	Review of cellulose and hemicellulose hydrolysis models			
Jensen *et al.* [27]	Mixtures of switchgrass, balsam, red maple, aspen, basswood	175	0.5 w/w% H_2SO_4	Biphasic, sequential hydrolysis of xylan

(*continued*)

Table 6.5   (*Continued*)

Source	Biomass	Temperature (°C)	Acidifying agent	Model description
Kobayashi and Sakai [111]	*Fagus crenata* Blume	74–147	1–16% H_2SO_4	Biphasic, sequential hydrolysis of xylan
Lloyd and Wyman [122]	Corn stover	140	0.68–1.0% H_2SO_4	Depolymerizaton of xylan; includes oligomer intermediates
Lu and Mosier [123]	Corn stover	150–170	0.05–0.2 M $C_4H_4O_4$	Saeman sequential hydrolysis of xylan; biphasic, sequential hydrolysis of xylan
Maloney *et al.* [21]	Paper birch	100–170	0.04–0.18 M H_2SO_4	Biphasic, sequential hydrolysis of xylan; release of acetyl groups
Mok *et al.* [85]	Whatman paper no. 1 and 42	190–225	5 mM H_2SO_4	Sequential hydrolysis of cellulose
Morinelly *et al.* [124]	Aspen, balsam, switchgrass	150–175	0.25–0.75 w/w% H_2SO_4	Sequential hydrolysis of xylan; includes oligomer intermediates
Nimlos *et al.* [118]	Xylose	160	0.2 M H_2SO_4	Quantum mechanics model of xylose dehydration
Rose *et al.* [125]	Furfural	150–169	0.1 M HCl	Pseudounimolecular destruction of furfural
Saeman [86]	Cellulose	170–190	0.4–1.6% H_2SO_4	Sequential hydrolysis of cellulose and monomers
Tillman *et al.* [112]	Aspen	95–169	0.83 w/w% H_2SO_4	Biphasic, sequential hydrolysis of xylan with mass transfer of acid
Weingarten *et al.* [25]	Xylose	150–170	0.1 M HCl	Parallel dehydration of xylose
Williams and Dunlop [116]	Furfural	50–300	0.05–0.10 M H_2SO_4	Pseudounimolecular destruction of furfural

6.6   Conclusions

Biomass hydrolysis at low pH has played an important role in the long history of biomass conversion to fuels and chemicals. Low-pH reactions have been used to prepare a wide variety of biomass types including agricultural residues, grasses, hardwoods, and softwoods for subsequent conversion by biological and chemical routes as well as to make sugars, furfural, and other products directly. Acidifying agents and concentrations as well as reactor types, temperatures, and times have all been adjusted to accommodate differences in biomass types and downstream operations and objectives. Although downstream operations can vary considerably, the primary pretreatment goals are to maximize product yields, generate reactive intermediates such as enzymatically digestible solids, sugars, or furfural, and avoid generation of compounds that would negatively influence downstream operations.

As the emphasis in biomass hydrolysis evolved from the recovery of sugars from cellulose to the removal of hemicellulose to prepare biomass for subsequent acid-catalyzed cellulose hydrolysis and later enzymatic hydrolysis of cellulose, pretreatment objectives have shifted from the recovery of glucose for fermentation to the recovery of hemicellulose-based sugars and modification of cellulose for enzymatic hydrolysis. Sulfur dioxide and sulfuric acid have been the most-studied catalysts for biomass pretreatment prior to biological conversion. Most SO_2 systems used batch reactors and steam explosion. Sulfuric acid has been used in batch, percolation, steam explosion, and two-stage batch pretreatments. Other acids such as nitric, phosphoric, and hydrochloric have been occasionally studied.

Recent interest in producing chemicals or "drop-in" hydrocarbon fuels has brought renewed attention to the complete hydrolysis of hemicellulose and cellulose to sugars and their subsequent reaction to organic

aldehydes and acids that can be catalytically converted to hydrocarbons. Although not traditionally referred to as pretreatment, these acidic reactions function in the same manner as traditional pretreatments, that is, production of reactive intermediates for subsequent conversion. Possible goals of these non-traditional pretreatments include maximizing production of furfural, levulinic acid, or carbohydrate-rich liquids. Another approach to fuels production is to combine hydrolysis with hydrogenation over a metallic catalyst to produce sugar alcohols.

Most models of cellulose and hemicellulose hydrolysis have been developed assuming a series of first-order homogeneous reactions in which the carbohydrate polymer is converted to monomers and then to degradation products. These models have been modified to account for parallel degradation pathways, the formation of oligomer intermediates, and differences in substrate reactivity. There are also several novel models describing hydrolysis, including the severity parameter and mass-transfer models. However, due to the empirical nature of existing models, their predictions must be validated if they are to be used with confidence.

Acknowledgements

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