Lignocellulose Pretreatment Using Acid as Catalyst

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Contents

Abstract

Pretreatment is a prerequisite step for bioconversion of lignocellulose into liquid biofuels and chemicals. Among the numerous developed pretreatment methods, acid-catalyzed pretreatment belongs to the predominant technologies which can effectively destroy the rigid structure of lignocellulose and greatly enhance the conversion of cellulose and hemicellulose. This chapter reviewed the current progress in lignocellulose pretreatment using acid as catalyst, including inorganic acids (sulfuric acid, SO_2, phosphoric acid, HCl, and nitric acid) and organic acids (oxalic acid, maleic acid, and organic acids assisted fractionation), and stressed

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the novelty and importance of the dry acid pretreatment (DryDA) and the commercial applications of these pretreatment technologies in the established commercial cellulosic ethanol plants.

Keywords

Lignocellulose pretreatment · Recalcitrance · Inorganic acids · Organic acids · Dry acid pretreatment (DryDA) · Dry acid pretreatment and biodetoxification (DryPB)

Background

Lignocellulosic biomass is a promising alternative feedstock for liquid biofuels and bio-based chemicals production due to its relatively low cost, great abundance, and sustainable supply [1]. In the twentieth century, acid hydrolysis, mainly concentrated sulfuric acid hydrolysis, was directly used to convert lignocellulose into monomer sugars and then further fermented into biofuels or chemicals [2–4]. The concentrated acid hydrolysis always involves two stages: a decrystallization stage to break down the crystal structure of fiber using sulfuric acid with more than 60% concentration and a hydrolysis stage with acid of around 20–30% concentration to liberate sugars from the decrystallized fiber [5]. Although the glucose yield of 72–82% can be achieved using the concentrated acid hydrolysis technology, major drawbacks including high cost of acid recovery, serious corrosion to the reactor materials, excess degradation of glucose and xylose into inhibitory compounds, a large amount of neutralizing agents usage, and gypsum disposal significantly affect the process economics [6, 7].

After World War II, a new process involving pretreatment and enzymatic hydrolysis was proposed with the finding of cellulase [8]. This process is viewed as the most viable strategy especially after the big achievement obtained in cellulase production cost reduction, since enzymatic hydrolysis of lignocellulose offers several advantages such as higher yield, lower by-product formation and energy requirement, mild operation condition, and environmental benign processing compared to acid hydrolysis. However, native lignocellulose is recalcitrant to degradation from microbes and enzymes due to its physical features and chemical structures. Pretreatment is thus an essential step to overcome the biorecalcitrance of lignocellulose and increase the yield of fermentable sugars from the following enzymatic hydrolysis step [9, 10]. Numerous pretreatment methods (including physical, chemical, physicochemical, and biological pretreatment) have been developed and demonstrated their effectiveness to facilitate the cellulose conversion in the lab. Among them, dilute acid pretreatment is one of the leading pretreatment technologies and has been commercialized in several established cellulosic ethanol plants [11–16]. In this chapter, we will discuss the current progress in pretreatment technologies using acid as catalyst, their advantages and disadvantages, and commercial applications in the established 2G ethanol plants.

Acid Pretreatment Using Inorganic Acids as Catalysts

Dilute acid pretreatment using inorganic acids as catalysts almost completely hydrolyzes hemicellulose, disrupts lignin structure, and partially solubilizes crystalline cellulose. The pretreatment is operated at a relatively high temperature (100–250 °C) and moderate pressure (<1.5 MPa), irrespective of the types of acids used. After dilute acid pretreatment, cellulose conversion in the enzymatic hydrolysis usually reaches higher than 90% due to hemicellulose removal [7, 10, 13, 14]. In this section, dilute acid pretreatment with sulfuric acid, SO_2, phosphoric acid, nitric acid, and hydrochloric acid as catalyzing reagents will be reviewed.

Sulfuric Acid Pretreatment

Dilute sulfuric acid pretreatment is a well-studied pretreatment method, which can significantly reduce lignocellulose recalcitrance and has shown its effectiveness on a wide range of feedstock, including softwoods, hardwoods, herbaceous crops, and agricultural residues [17–22]. Dilute sulfuric acid pretreatment is usually performed over a temperature range of 140–210 °C, with sulfuric acid concentration less than 4 wt% and residence time from a few minutes to hours in different types of pretreatment reactors [22–27]. The solids loading of lignocellulose during pretreatment is usually less than 10 wt% to ensure a sufficient impregnation of aqueous acid to the solid material. To maximize sugar recovery and enhance biomass digestibility, a two-stage dilute acid pretreatment including a low severity (low temperature, low acid concentration) dilute acid pretreatment to promote hemicellulose hydrolysis/recovery in the first stage and a high severity second stage to hydrolyze a portion of the remaining cellulose to glucose was proposed by Nguyen et al. [28]. Bhagia et al. reported a flow-through pretreatment with very dilute acid (0.05 wt%) to enhance cellulose digestibility because of more lignin removal compared to the batch pretreatment [29]. Wang et al. compared the effect of reactor types (ZipperClave, Steam Gun, and Horizontal Screw) on pretreatment efficiency under the same nominal conditions and found that the Horizontal Screw reactor achieved a much higher cellulose digestibility (95%) compared with the Steam Gun (88%) and ZipperClave reactor (68%) because of the mechanical grinding effect imposed by the Horizontal Screw reactor during pretreatment [30].

In a technical report issued by NREL (National Renewable Energy Laboratory) in 2011, the commercial cellulosic ethanol plant was designed to handle 2000 metric ton of dry corn stover per day [31]. Dilute sulfuric acid pretreatment included a steam-heating and acid impregnation stage operated at 100 °C for 10 min in a vertical presteamer and a pretreatment stage operated at 158 °C with sulfuric acid concentration of 1.8 wt% for 5 min in a single horizontal reaction vessel. The conversion ratio of xylan to xylose reached higher than 90% in pretreatment, while the conversion ratio of glucan to glucose also reached higher than 90% in the following enzymatic hydrolysis [31].

SO_2-Catalyzed Steam Pretreatment

Steam pretreatment after SO_2 impregnation is another effective method to hydrolyze hemicellulose sugars and soften the structure of cellulose to enhance enzymatic digestibility of lignocellulose [32–34]. Like dilute sulfuric acid pretreatment, impregnation of lignocellulose with SO_2 is the prior step before feeding it into the high-temperature steam pretreatment reactor. The optimum pretreatment conditions using SO_2-catalyzed steam explosion for lodgepole pine were determined to be 200 °C, 5 min with 4 wt% SO_2. Simultaneous saccharification and fermentation (SSF) of the pretreated lodgepole pine provided an overall ethanol yield of 77%, corresponding to 244 g ethanol/kg raw material [35]. In order to enhance the enzymatic digestibility of the pretreated softwood, a two-step steam pretreatment was developed. In the first step, softwood was impregnated with 3.0 wt% gaseous SO_2 and steam pretreated at low severity (190 °C for 2 min) to hydrolyze the hemicellulose and release the sugars into the solution. In the second step, the washed solid material from the first step was impregnated once more with 3.0 wt% gaseous SO_2 and steam pretreated under more severe conditions (220 °C for 5 min) to enhance the enzymatic digestibility. The overall sugar yield after enzymatic hydrolysis reached 80%, which was a little higher compared to one-step steam pretreatment [36]. However, the difficulty with separation and washing of the material at high pressure between the two pretreatment steps was a major drawback. A new one-step pretreatment was developed, in which the temperature was varied stepwise at two levels. The ethanol yield of 74% was achieved when running the pretreatment as one-step, two levels of temperature (190 °C for 2 min and 210 °C for 5 min). But the inhibitors might be a litter higher due to the presence of monomer sugars after a lower severity pretreatment [37]. SO_2-catalyzed steam pretreatment is also effective on agricultural residues, such as corn stover [38].

Phosphoric Acid Pretreatment

Phosphoric acid is apparently more expensive than sulfuric acid but may provide a coproduct (phosphate) as a nutrient ingredient for the fermenting microorganisms. Initial studies concerning animal feeds have shown that the hemicellulose of ryegrass straw can be hydrolyzed with phosphoric acid [39]. The optimum pretreatment conditions using wheat bran were acid concentration of 1.75 wt%, 190 °C for 10 min. This pretreatment was also scaled up to a 30 L vertical plug-flow continuous reactor in a demo plant in Sweden. Enzymatic hydrolysis of pretreated slurry reached a polysaccharides yield of 85%. Compared to the untreated bran biomass, an increase of 51% was observed in the ethanol yield following pretreatment (a total ethanol yield of 95%) [40].

More recent studies have demonstrated that the hemicellulose component in corn stover [17], sugarcane bagasse [41, 42], sorghum straw [43], and wheat straw [44, 45] can be effectively hydrolyzed in solutions containing 2–6 wt% phosphoric acid at 100–122 °C, which can greatly facilitate the cellulose conversion in the enzymatic hydrolysis [46, 47].

Other Inorganic Acid-Catalyzed Pretreatment

Besides sulfuric acid, SO_2, and phosphoric acid, hydrochloric acid and nitric acid have also been used as catalysts for pretreatment. Toquero and Biolado pretreated the dry wheat straw with 1.5 wt% hydrochloric acid solution at a solid/liquid ratio of 1:10 (w/w) for 5 min in a 500 mL screw cap bottle and then autoclaved at 121 °C for 60 min. Most xylose (16.49 g/100 g) was released, but large amounts of inhibitors (including furfural and HMF) were generated, which further led to a poor fermentation performance [48].

Similar to phosphoric acid, nitrate, formed upon being neutralized after nitric acid pretreatment, could be used as a nitrogen source for fermentation process. In a pretreatment condition of 0.65 wt% nitric acid, 158.8 °C for 5.86 min, a maximum xylose yield of 86.5% and a cellulose digestibility of 83.0% were achieved. The sugar solution that contained nitrate derived from the acid catalyst supported the enhancement of ethanol yield by *Pichia stipites* from 10.92 g/L to 14.50 g/L. It clearly revealed that nitric acid could be used not only as pretreatment catalyst but also as a nitrogen source in the bioethanol fermentation process [49]. Later on, the cellulose conversion was improved up to 93.0% when the nitric acid pretreatment was operated at 4 wt% nitric acid, 94–96 °C for 4 h [50].

Acid Pretreatment Using Organic Acids as Catalysts

Even though dicarboxylic acids such as oxalic acid and maleic acid are more expensive than inorganic acids, they still have been suggested as alternative catalysts for pretreatment [51–53]. This is because dicarboxylic acids exhibit a high catalytic efficiency, but unlike inorganic acids, they do not promote the degradation of free sugars to furfural and HMF [54]. Furthermore, generating gypsum and noxious odors during dilute sulfuric acid pretreatment could be avoided [55].

Oxalic Acid Pretreatment

Oxalic acid can catalyze the hydrolysis of hemicellulose and cellulose directly. It is one of the strongest organic acids known and is considerably stronger than acetic acid and somewhat stronger than H_2SO_3 as well. At the same time, oxalic acid is less toxic to yeasts and other microbes than acetic or sulfurous acids because its lower p*K*a restricts diffusion of the ionized form across cellular membranes. In comparison to H_2SO_3, it does not inhibit glycolysis and does not produce noxious odors [55–62]. Corncob pellets (80.6 kg dry matter) were impregnated with 3 wt% oxalic acid at a solid/liquid ratio of 1:6 in a 500 L reactor for 20 min, and then they were pretreated at

168 °C for 26 min. The highest ethanol production after SSF of washed solid biomass with *Scheffersomyces stipites* was 21.1 g/L [63]. Dilute oxalic acid was also used to pretreat maple wood to improve compatibility with downstream operations. The total xylose yield of −84% was obtained with 0.5 wt% oxalic acid pretreatment at 160 °C. The total glucose plus xylose yields of −85% was achieved after enzymatic hydrolysis [64]. Dilute oxalic acid also showed effective on the yellow poplar and giant reed biomass [65, 66]. Due to the high price of the oxalic acid, electrodialysis (ED) with potential of 10 V and pH 2.2 was used to recover and reuse oxalic acid after pretreatment. The recovery efficiency of oxalic acid from hydrolysates almost reached 100%. The power consumption to treat 1 mol of oxalic acid was estimated to be 41.0 wh. The highest ethanol production was 19.38 g/L (corresponding to the ethanol yield of 0.33 g/g) after 72 h SSF [67].

Maleic Acid Pretreatment

Maleic acid has also been tested as an alternative for sulfuric acid for pretreatment. Kootstra et al. found that the optimal pretreatment conditions for wheat straw were 170 °C for 50 min, with 46 mM maleic acid. During pretreatment, up to 90% of all xylan was converted to monomeric xylose. Almost complete conversion of glucan to glucose can be reached (90% from solids, 7–10% in pretreatment liquid) after enzymatic hydrolysis. The furfural formation was so limited that can be negligible [68]. Barisik et al. pretreated wheat straw using a lower maleic acid concentration (1.08%) but higher temperature (210 °C) for 19.8 min and obtained a satisfied ethanol yield (80%) [69]. In order to obtain a high concentration of products, high solids loading pretreatment (20 wt%) of rice straw with maleic acid was evaluated by Jung et al. [70, 71]. The highest enzymatic digestibility obtained was over 80%. After detoxification with activated carbon, SSF of the whole slurry generated a high ethanol yield of 62.8%. These findings suggested that high solids loading pretreatment using maleic acid and SSF of the whole slurry of pretreated rice straw can be combined to improve the process economics [70, 71].

Combination of Fractionation with Organic Acids

The concentrated formic acid and acetic acid have been used to solubilize the hemicellulose and lignin components in lignocellulose biomass, thus the digestibility of the cellulose retained in the solids is enhanced [72]. But acylation of cellulose takes place during formic acid (formylation) or acetic acid (acetylation) pretreatment. An additional deformylation or deacetylation with alkali is usually needed [72].

A lignocellulose pretreatment process was developed with formic acid delignification (FAD) followed by alkaline deformylation (AD), which was termed as Formiline process. More than 80% of lignin and hemicellulose were removed during pretreatment. The final ethanol concentration was 80.1 g/L at an initial solid consistency of 20% [72, 73]. Formic acid was also used separately to fractionate the hemicellulose and lignin in corn stover. The retention yield of cellulose and extraction yields of hemicellulose and lignin were 89.5%, 79.8%, and 65.6%, respectively, after pretreatment with 88 wt% formic acid, at a solid/liquid ratio of 1:13, 80 °C for 3 h. The enzymatic hydrolysis rate of glucan and xylan could reach 62.8% and 79.4%, respectively [74].

Acetic acid (AA)-catalyzed liquid hot water (LHW) pretreatment on raw corn stover (RCS) was carried out at 195 °C for 15 min with acetic acid concentrations between 0 and 400 g/kg RCS. The highest glucan recovery was found to be 97.42% when 15 g AA/kg RCS was employed. After enzymatic hydrolysis and fermentation, the ethanol concentration of 33.72 g/L was obtained, higher than 22.04 g/L from the non-catalyzed LHW pretreatment (195 °C for 15 min) [75]. The optimal conditions for the hydrogen peroxide-acetic acid (HPAC) pretreatment were 80 °C, 2 h, and an equal volume mixture of H_2O_2 and CH_3COOH. After HPAC treatment, 97.2% of the lignin was removed. Fermentation of the hydrolysate after enzymatic hydrolysis by *Saccharomyces cerevisiae* resulted in an ethanol yield of 85.0% [76].

However, these studies have been performed only in a laboratory level, largely because of the high price of the organic acids or the high cost of organic acids recovery. In addition, the corrosivity of formic/acetic acid makes them less attractive than the alcohol-based fractionation [72].

A New Variant of Dilute Acid Pretreatment: Dry Acid Pretreatment (DryDA)

A major common shortcoming of the present dilute acid pretreatment is the low solids loading of lignocellulose because of low bulk density and super water absorbability, which will generate several serious problems:

(1) A large amount of wastewater is released and will cause a heavy burden on wastewater treatment.
(2) A considerable amount of fine feedstock solid particles and sugars are lost in the following solid–liquid separation operation, which decreases the overall fermentable sugars yield.
(3) The three main components of lignocellulose are easy to be degraded into inhibitory compounds in presence of the aqueous acids.
(4) High capital investment due to low processing capacity of pretreatment reactors.
(5) High corrosion speed of the pretreatment reactors [11].

Therefore, pretreatment at high solids loading (higher than 20 wt%) without affecting the pretreatment efficiency seems promising to solve the abovementioned problems. However, the mixing and mass/heat transfer challenge the high solids loading pretreatment.

In order to operate the pretreatment at a high solids loading, a dry dilute acid pretreatment (DryDA) was developed in East China University of Science and

Technology [77–82], which was originally dependent on two measures of high lignocellulose solids to liquid sulfuric acid ratio (1:1 to 2:1) and the full feedstock filling ratio to the pretreatment reactor. This novel pretreatment produces a “dry” pretreated substrate (moisture content is higher than 50%) without any aqueous acid-containing wastewater generation while maintaining a satisfactory pretreatment efficiency with a broad substrates spectrum (including corn stover, rice straw, wheat straw, cotton stalk, and rape straw) [77]. Later on, to enhance the mixing and mass transfer during pretreatment, the helical ribbon reactor including a helical ribbon stirrer mounted on the shaft and a bottom anchor stirrer to avoid sedimentation of the solid lignocellulose particles was developed. The computational fluid dynamics (CFD) simulation showed that mixing between hot steam and the solid materials was greatly enhanced compared to that in an empty cylinder reactor (without mixing impeller) [78]. Also, the inhibitor generation was reduced significantly. It was worth noting that the labor-intensive and time-consuming presoaking operation before pretreatment can be completely removed in the newly designed pretreatment reactor. The solid feedstock and the liquid acid can be fed into the reactor cocurrently by helically agitation, and a homogeneous mixing state could be reached within a few minutes [79]. The corrosion of pretreatment reactor metal walls was also significantly reduced using DryDA, in which the aqueous dilute acid solution was completely absorbed by high solids corn stover feedstock. The reactor corrosion was reduced by approximately 85% when the solid/liquid ratio increased from the conventional value of 1:10 to the high value of 2:1 at the same sulfuric acid concentration in the DryDA [80]. Another advantage of DryDA is that the low pH of the pretreated lignocellulose and the relative higher content of inhibitors create a favorable antimicrobial contaminant environment to make the long storage of the pretreated materials become true without microbial contamination [81]. Now, the batch pretreatment reactor has been scaled up to 2.5 M^3 to produce pretreated agricultural residues for the following enzymatic hydrolysis to produce sugar syrup (1000 t per year) in Caixin Sugar Industry Co. (Dancheng, Henan, China) [82]. In the future, the continuous dry dilute acid pretreatment needs to be developed to enhance the pretreatment productivity.

Energy consumption and wastewater generation are among the determinant factors on overall cost and technology penetration into fuel ethanol industry. A strict Aspen Plus model for the dry acid pretreatment and biodetoxification (DryPB) biorefining process was established to calculate the water and energy balance. DryPB minimized the steam consumption to 8.63 GJ and wastewater generation to 7.71 t in the core steps of biorefining process for production of 1 metric ton of ethanol, lower than those of conventional dilute acid pretreatment (11.21 GJ in steam consumption and 16.58 t in wastewater generation) and much close to those of corn ethanol production (7.83 GJ in steam consumption and 8.33 t in wastewater generation). It clearly indicated the advantages of DryPB over DAP and implied that the technical gap between cellulosic ethanol and corn ethanol has been almost filled up [83].

Commercial Applications of Dilute Acid Pretreatment

Tremendous advances have been made by the lignocellulose biorefining industry. Several commercial cellulosic ethanol production plants, which use dilute acid pretreatment technologies, have been inaugurated in the past few years [84]. On September 3 of 2014, POET-DSM Advanced Biofuels, LLC, announced that the first commercial-scale cellulosic ethanol plant (20 million gallons per year) opened for business (http://www.dsm.com). In the POET-DSM process, a two-stage dilute sulfuric acid pretreatment was employed to degrade hemicellulose and partially depolymerize lignin [84]. Later, in 2014 (October 17), Abengoa celebrated their cellulosic ethanol plant's grand opening, which is based in Hugoton, Kansas, and when at full scale will produce 25 million gallons of cellulosic ethanol from biomass per year as well as 21 MW of electricity. In Abengoa's process, a dilute sulfuric acid-catalyzed steam explosion pretreatment was used to degrade the hemicellulose and facilitate the following enzymatic hydrolysis (http://www.abengoa.com). On July 22 of 2015, the Raizen Corporation in Brazil, one of the world's largest producers of sugarcane ethanol, launched Iogen Energy's cellulosic ethanol technology (40 million liters of cellulosic ethanol a year from sugarcane bagasse and straw) in Piracicaba, Sao Paulo. In the Iogen process, the feedstock was pretreated using dilute acid method (0.5–1% sulfuric acid, 200–250 °C for less than 1 min). This technology has extensively proven (24 h a day, 7 days a week, from 2007 to 2012) in Iogen's Ottawa, Canada, demonstration facility (http://www.iogen.ca) [8]. For the other two companies, Beta Renewables and DuPont, steam explosion and aqueous ammonia pretreatment technologies have been commercialized in their own cellulosic ethanol plants in North America, respectively [84].

In China, Shandong Longlive Biotechnology Co. (Yucheng, Shandong) was authorized by the Chinese government to produce 50,000 t/annum of cellulosic ethanol using corncob residues after dilute acid pretreatment for xylitol production (http://www.longlive.cn) in 2012. In the same year, it started to provide fuel ethanol to petrochemical companies.

Even though the abovementioned companies declared the opening of their commercial cellulosic ethanol plants, they are still in their current start-up phase with different levels of operation. At least a few years are needed to overcome all the issues encountered that have prevented full operation [84].

Conclusion

Dilute sulfuric acid pretreatment has been applied to the current commercial cellulosic ethanol plant because of its effectiveness on different kinds of lignocellulose, using the cheap sulfuric acid as catalysts, and easy scale-up, but the current big challenge is to enhance process versatility to be able to deal with more than one raw material at a time [84]. DryDA is the most promising pretreatment method for its high solids loading, lower wastewater generation, lower energy input, lower corrosion to the pretreatment reactor, easy optimization to deal with different substrates, and long-term storage without microbial contamination and fire risks. However, the continuousness of DryDA and the scalability of the helical stirring impeller need to be solved before used in the commercial plants. The other dilute acid pretreatments, based on different types of inorganic acids, organic acids, or the organic acid assisted fractionation, are still at a bench-scale investigation. There is a long way for them to be used in the industry.

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