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MINI REVIEW

Recent progress on the pretreatment and fractionation of lignocelluloses for biorefinery at QIBEBT

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ABSTRACT

Pretreatment and fractionation are amongst the key steps for the conversion of lignocelluloses to sustainable biofuels, biomaterials or biochemicals, as pretreatment/fractionation can break the natural recalcitrance of lignocelluloses, improving the conversion efficiency of downstream processes. This paper reviews the recent progress on the pretreatment and fractionation of lignocelluloses for biorefinery at the Chinese Academy of Sciences - Qingdao Institute of Bioenergy and Bioprocess Technology (QIBEBT). The main technologies developed at the QIBEBT in recent years include alkaline twin-screw extrusion pretreatment, modified alkali pretreatment, hydrogen peroxide-assisted sodium carbonate pretreatment, fractionation with formic acid, as well as the two-step fractionation by hot water treatment coupling ammonium sulfite treatment. With the development of these technologies, a pilot scale platform for the pretreatment and saccharification of biomass has been established in the pilot plant of QIBEBT.

Keywords: Biomass; Pretreatment; Fractionation; Sustainable biofuels; Value added products

1. INTRODUCTION

Environment and energy crises are the major issues that human being face and should be well solved in the 21st century.[1] Therefore, it is extremely urgent to develop green and cost-effective technologies to produce sustainable fuels, materials and chemicals. Biomass feedstock is the only source of sustainable organic compounds. In China, over 700 million tons of agricultural waste (e.g. corn stover and wheat straw) can be produced annually.[2] Hence, efficient utilization of lignocelluloses (including wood, agricultural waste, energy plants, etc.) is of critical importance for the sustainable development of human society.

As known, to achieve efficient utilization of lignocelluloses, pretreatment and fractionation are highly needed to break the natural resistance of lignocellulosic biomass.[2-3] Up to now, many pretreatment technologies including physical, biological, chemical (e.g. dilute acid, dilute alkali, ionic liquid, etc.), and multiple/combined pretreatment (e.g. steam explosion, sulfite pretreatment to overcome recalcitrance of lignocellulose (SPORL), etc.) have been investigated on various feedstocks and are still in development. [4-5]

In this paper, the recent technologies for the pretreatment and fractionation of lignocelluloses developed at the Chinese Academy of Sciences - Qingdao Institute of Bioenergy and Bioprocess Technology (QIBEBT) are briefly reviewed.

2. ALKALI-BASED PRETREATMENT

Alkali-based pretreatment is generally believed to be one of the most promising pretreatment technologies, mainly because 1) alkali-based pretreatment can efficiently remove lignin and various uronic acid substitutions on hemicelluloses with relatively low loss of fermentable sugars in comparison with acid or hot water pretreatment,[2, 4] and 2) alkali-based pretreatment can be integrated with alkali-based pulp mills by using the equipment (e.g. cooking digester, disc refiner, etc.) and chemical recovery and waste water treatment systems already well-developed in pulp industry to reduce the capital cost of pretreatment and gain more benefits for pulp mills.[6-7]

2.1 Alkaline twin-screw extrusion pretreatment

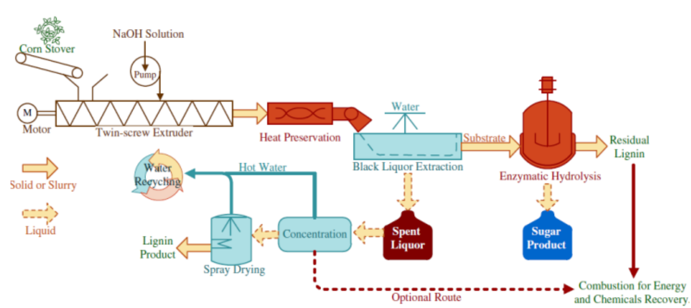

Fig. 1 Schematic diagram of the overall ATSE pretreatment system

A pilot scale alkaline twin-screw extrusion (ATSE) pretreatment system was set up in a QIBEBT pilot plant in collaboration with SHELL Company. Shown in Fig. 1 is the schematic diagram of the overall pilot scale ATSE pretreatment system. In pilot-plant scale trials, the feedstock was added in the twin-screw extruder through a feeding inlet. During extrusion, two screw extruders were co-rotated intermeshing with each other. Each screw extruder consisted of four transport screw elements (TSEs) and four reversed screw elements (RSEs) (Fig. 2). Via the action of the TSEs, the biomass was pushed to the RSEs with the opposite pitch of threads to the TSEs. After crushed by the force of transporting, mixing, and grinding, the substrate was pushed to pass through the skewed slots of the RSEs. The repeated squeezing and crushing then occurred when the biomass was delivered to the subsequent TSE and RSE sections.[8] At last, the biomass was completely crushed and the fibers were separated and delaminated, leading to a size reduction and an increase in the external/internal specific surface area of biomass.[5] Also, with the addition of alkali, the efficient chemical reactions could lead to effective lignin removal. Thus, the biomass digestibility and final total sugar yields could be improved.[8]

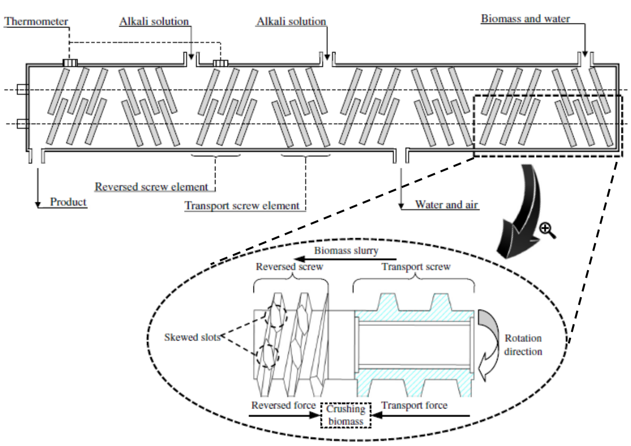

Fig. 2 Schematic diagram of the novel twin-screw extruder

The rotational speed of extruder could be adjusted and the screw configuration can be specially designed and adjusted by arranging the pitches, lengths, stagger angles, positions, and the ratio of TSE to RSE, to match the properties of feedstock.[9] In the trials, the screw speed was fixed at 325 rpm, and the capacity of the extrusion machine was 200 kg/h. Also, the corresponding extrusion duration and energy consumption were about 30 seconds and 240 kWh/t biomass, respectively. The energy consumption of ATSE pretreatment was lower compared to steam explosion and SPORL pretreatment methods.[10, 11] Results of the pilot trials showed that, with the supplement of 6% NaOH, the liquid to solid (L/S) ratio of 2:1, and keeping warmth (after extrusion) for 1 h, about 71% of lignin could be removed, and the final total sugar yields could reach up to 78%. In this case, 317 g glucose and 150 g xylose could be obtained after ATSE pretreatment of 1 kg corn stover and enzymatic saccharification.[8] Comparable results could also be obtained by treating wheat straw or rice straw as the feedstock.

The advantages of ATSE pretreatment include (1) no need for severe size reduction of biomass before pretreatment; (2) low water usage; (3) no need for extra heating equipment; (4) no inhibitors generated for the downstream fermentation. It was reported that, the overall acetone-butanol-ethanol (ABE) yield was 0.112 g/g corn stover, and no inhibitors to ABE fermentation of ATSE pretreated corn stover.[12]

2.2 Modified alkali pretreatment

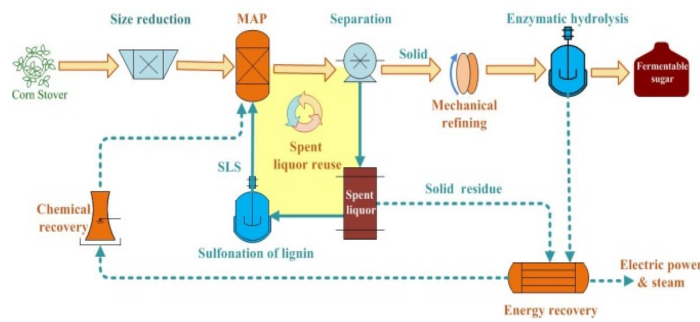

Fig. 3 The overall flow sheet of modified alkali pretreatment process

Fig. 3 presents the overall process of modified alkali pretreatment (MAP). The MAP process was established on the basis of the on-line production and utilization of sodium lignosulfonate (SLS) at both lab and pilot scale. SLS was produced by direct sulfonation of spent liquor. The produced SLS was then reused as a surfactant to promote chemical (such as anthraquinone (AQ)) penetration and lignin removal in the next cycle of MAP process, thus improving the enzymatic digestibility of pretreated corn stover.[13] In this case, part of the spent liquor of the MAP process was more efficiently utilized. Compared to the conventional NaOH pretreatment, the MAP process could lower the NaOH dosage from 13-14% to 11%, and reduce the pretreatment temperature from 140 ºC to 120 ºC to achieve about 80% of final total sugar yield. Under the optimal MAP conditions (11% NaOH charge, 2% SLS, 0.1% AQ, 120 ºC for 40 min, L/S = 6), the delignification rate and final total sugar yield could reach about 78% and 80%, respectively, which were about 6% and 9% higher in comparison with the blank conventional NaOH pretreatment under the same conditions. It was also found that the sulfonation degree of SLS had linearly impact on the final total sugar yields (Fig. 4).[13]

On the other hand, the impact of the key factors was investigated on the enzymatic saccharification of the MAP treated corn stover.[13, 14] Results showed that the suitable pH for achieving high xylan yield was in the range of 4.0-4.7, and the highest final total sugar yield was obtained at pH 4.4. This phenomenon was due to the fact that the optimum pH for xylanase to work efficiently with cellulase was around 4.4 under the conditions. In addition, the supplement of xylanase or surfactant (like SLS) could promote the enzymatic saccharification by reducing the nonspecific binding of cellulose.[14] This project was completed in collaboration with P&G Company.

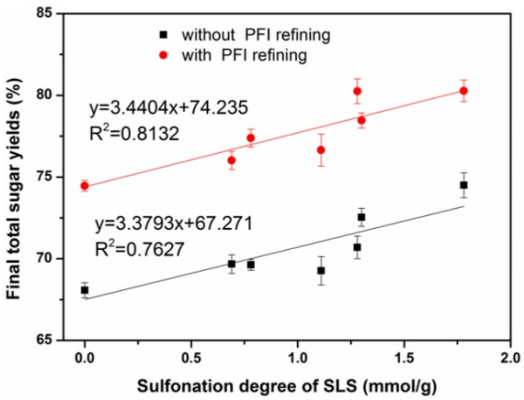

Fig. 4 Effect of the sulfonation degree of SLS on the final total sugar yield

2.3 Hydrogen peroxide-assisted sodium carbonate pretreatment

As known, Na_2CO_3-based pretreatments are more suitable for herbaceous biomass and agricultural waste, compared to woody biomass, despite the effectiveness of Na_2CO_3 pretreatment may be lower than NaOH pretreatment under the same conditions.[2] Na_2CO_3 pretreatment can be conducted in the range of 70-180 ºC, and the reaction time can be extended to a couple of hours, depending on the process used and the properties of the raw materials.[2, 15]

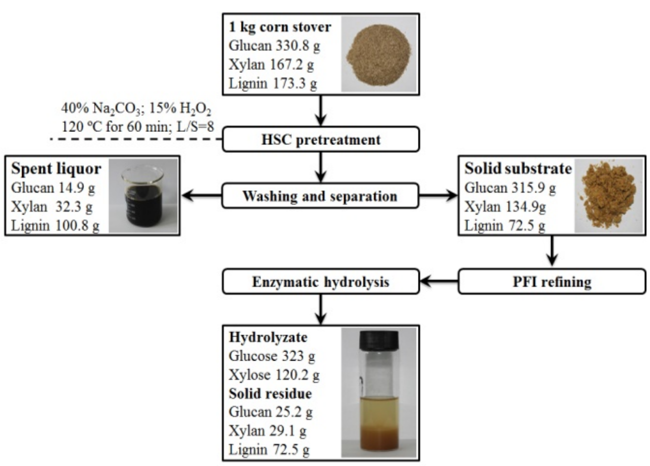

Fig. 5 Mass balance of H_2O_2-assisted Na_2CO_3 pretreatment

To promote lignin removal, we added H_2O_2 in the Na_2CO_3 pretreatment and established a H_2O_2-assisted Na_2CO_3 (HSC) pretreatment process in lab scale. It was found that the addition of H_2O_2 in Na_2CO_3 pretreatment could not only enhance lignin removal but also increase the hydrophilicity of the residual lignin, leading to the improved enzymatic saccharification and the yield of fermentable sugars. [15] Also, post mechanical refining could further improve the enzyme accessibility by increasing porosity of substrates. [16] After HSC pretreatment (40 wt % Na_2CO_3 and 15 wt % H_2O_2, 120 ºC for 60 min) and enzymatic hydrolysis, the final total sugar yield could achieve 79%, which was about 10% higher in comparison with the conventional Na_2CO_3 pretreatment under the same conditions. The corresponding mass balance of HSC pretreatment is displayed in Fig. 5. HSC pretreatment will have less environmental impact, less barriers for large scale production, and the recovery of Na_2CO_3 does not require a causticizing stage.[15]

3. FRACTIONATION OF LIGNOCELLULOSE

The main components of lignocelluloses could be utilized better and more efficiently by suitable fractionation (including alkali-based pretreatment).[17] Through the development of high-value added products, the feasibility of pretreatment/fractionation at commercial scale could be highly improved. [2]

3.1 Formic acid fractionation

Previously, we developed a fractionation method by the use of formic acid (FA) of 88% concentration (commercial grade). The overall process of FA fractionation of corn stover is given in Fig. 6.

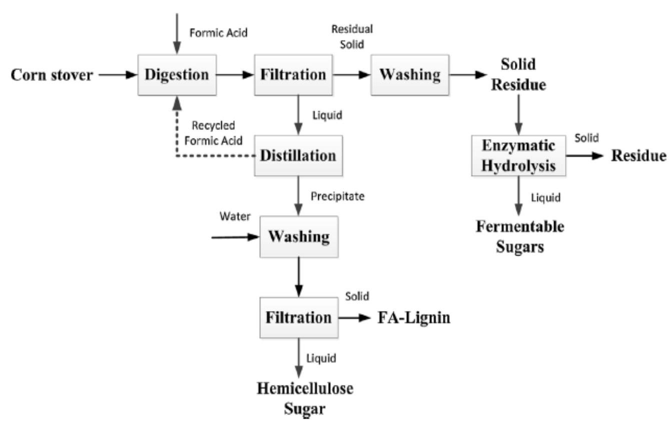

Fig. 6 The flowchart of formic acid fractionation of corn stover

The corn stover went to digester to be digested with FA. Upon completion of the reaction (80 ºC for 3 h), the stock was subjected to filtration to separate the cellulosic pulp fibers and liquid containing the dissolved lignin and hemicelluloses. Through the distillation, FA could be recovered from the liquid, and the precipitate went to washing. During washing, hemicelluloses could be dissolved while lignin was still in solid phase. Thus, hemicelluloses and lignin could be further separated via filtration. After washing of the separated cellulose-rich pulp, it could be subjected to enzymatic hydrolysis to produce fermentable sugars. After FA fractionation, the recovery rates of cellulose, hemicelluloses, and lignin could reach to 89.5%, 79.8% and 65.5%, respectively.[18]

Currently, we collaborated with Boeing Company working on the FA fractionation of pine wood. A set of pilot FA fractionation system was built in our pilot plant. Under the optimized conditions (pine wood particle size < 5 meshes, L/S ratio of 6:1, dosage of H_2O_2 of 5%, FA concentration of 88%, 140 ºC for 40 min), the yields of cellulose, hemicelluloses, and lignin reached to 87.7%, 83%, and 82.5% respectively. The purity of cellulose could be improved to 94% by further bleaching with H_2O_2, and the purity of lignin could be over 90%. The addition of H_2O_2 could promote lignin separation. In addition, economic evaluation of the scaled-up FA fractionation system was conducted (with the capacity of 10^5 tons feedstock), and the sensitivity analysis showed that the FA recovery yield was the most important factor, which should be well handled during large scale production.

3.2 Produce xylo-oligosaccharides (XOS) and glucose from corn cob

Corn cob is an inexpensive and abundant resource of hemicellulose, which can be used to produce xylo-oligosaccharides (XOS), xylose, furfural, or other xylose-based products.[17] Among them, XOS are widely used as food and feed additives, which are considered soluble dietary fibers, because XOS as the value added products have prebiotic activity, favoring improvement of bowel and immune functions, antimicrobial properties, and other health benefits.[19]

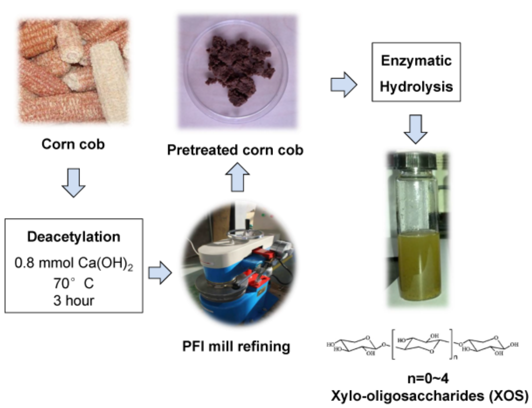

Fig. 7 Process of XOS production from corn cob

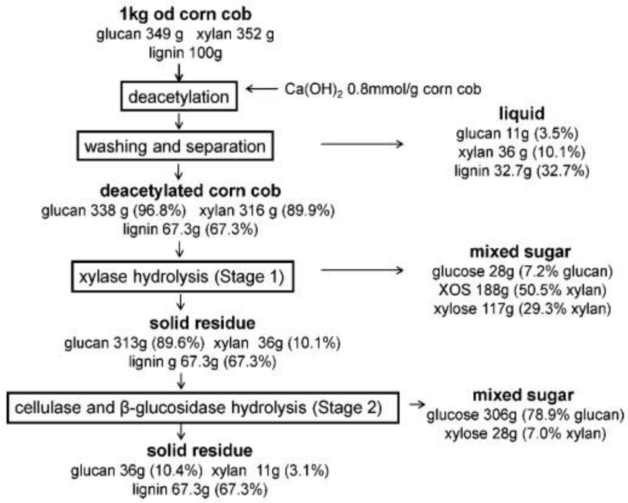

Fig. 8 Mass balance of the overall process for the production of XOS and glucose from corn cob

Therefore, we developed a two-stage enzymatic hydrolysis process to produce XOS and glucose from corn cob, separately. In order to improve enzymatic digestibility, the pretreatment of deacetylation plus mechanical refining (PFI refining) was conducted, as shown in Figs. 7 and 8. As known, the content of acetyl group was one of important factor to hinder the enzymatic hydrolysis of substrate.[5] It was found that $Ca(OH)_2$ could be the most suitable alkali for deacetylation in this work, compared to NaOH and Na_2CO_3.[20] Also, post PFI refining could further enhance the enzymatic digestibility of substrate, and the increased extents of sugar yields ranged from 0.023 to 0.212 g/g of corn cob.[20] The improvement was in good agreement with the results presented in Fig. 4.

Shown in Fig. 8 is the mass balance of overall process for the production of XOS and glucose from corn cob. As displayed in Fig. 8, after lime deacetylation (with lime dosage of 0.8 mmol/g-substrate) and PFI refining, 79.8% xylan was hydrolyzed in 1st stage of the enzymatic hydrolysis and 50.5% hemicellulose was converted to XOS. The cellulose in the solid residue separated from the 1st stage could be highly digested by cellulase and β-glucosidase in the 2nd stage. In total, 86.8% of xylan and 86.1% of glucan in the raw corn cob were hydrolyzed in the two-stage enzymatic saccharification. The results obtained indicated that the combined lime deacetylation and PFI refining pretreatment process was a relatively effective approach to enhance the enzymatic digestion of corn cob. On the other hand, the two-stage hydrolysis (also like a fractionation) can make the resultant sugar products simpler and easier to be used in the downstream processes, in comparison with the traditional one-stage enzymatic hydrolysis.[20]

3.2 Fractionation by hot water treatment coupling ammonium sulfite treatment

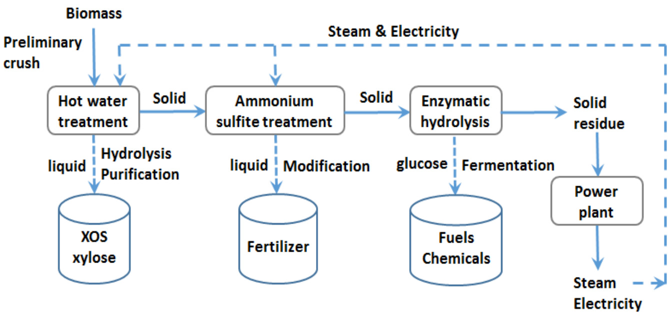

Fig. 9 The whole process of HW + AS fractionation

Hot water (HW) treatment is an effective method to separate hemicelluloses,[21] and ammonium sulfite (AS) treatment can efficiently remove lignin.[22] Hence, most recently, we coupled HW treatment with AS treatment to do the fractionation of wheat straw (Fig. 9). Results showed that over 80% hemicelluloses could be separated in HW treatment (175 ºC for 20 min) and the delignification rate of lignin during AS treatment (160 ºC for 1 h) was higher than 80% as well. After the two-stage fractionation, the separated hemicelluloses could be used to produce XOS and the yield of XOS after xylanase hydrolysis was higher than 65%. The separated lignin-rich liquor could be modified to lignin-based fertilizer, while the separated cellulose-rich stock could be subjected to enzymatic hydrolysis to produce glucose, which could be further fermented to biofuels (e.g. ethanol, butanol) or chemicals (e.g. succinic acid, isoprene) to increase the economic feasibility of whole process for large scale production. In order to further lower the cost of this process, this two-stage fractionation technology could be integrated with a power plant by utilizing the surplus steam and electricity. The separated solid residue from the WH + AS fractionation process could be utilized by the power plant to generate green electricity (Fig. 9). The whole process is green and sustainable with the development of high value added products. Further studies of this project are under way with the aim for commercial applications.

4. CLOSING REMARK

It is of critical importance to develop green and cost-effective pretreatment and fractionation technologies for downstream conversion of lignocelluloses. In recent years, a number of novel technologies have been developed at CAS - QIBEBT, including ATSE pretreatment, MAP process, HSC pretreatment, FA fractionation, and the two-step fractionation of HW + AS technologies. A pilot scale pretreatment/fractionation and saccharification platform was established at the organization. This platform can handle more than 1000 tons of biomass annually, and about 20 kg fermentable sugars and 10 kg ethanol can be produced per day.

To further increase the economic feasibility of the whole process of lignocellulosic biomass conversion, it is essential to generate high value added products (besides biofuels). The pretreatment/fractionation process can be integrated with a pulp mill or a power plant to lower the overall cost of the process. Indeed, a rational process design of pretreatment/fractionation has to match the properties of the starting material, available resources, environment, process configuration, and the quality of the end-products.

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GRAPHIC ABSTRACT

The pilot scale pretreatment/fractionation and saccharification platform in QIBEBT

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