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Review

Clean production technology of integrated pretreatment for Lignocellulose

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Pretreatment is a key step for lignocellulose converting into universal raw material for industries as alternative of petroleum. This review discusses that single pretreatment lacks cost-competitiveness because only one product takes responsibility for all cost. Based on the inheterogeneity of lignocellulose and the advantages of steam explosion pretreatment, steam explosion integrated pretreatment is proposed as strategy to solve the problem above. Steam explosion integrates with different pretreatment technologies to deconstruct lignocelluloses selectively for multiple products. By comparison, steam explosion-washing-alkali extraction-mechanical carding integrated pretreatment is considered the best. Finally, industrial demonstration of this integrated pretreatment is given out. With this integrated process, the recovery yields of cellulose, hemicelluloses and lignin reached 70, 80 and 80%, respectively.

Key words: Clean production technology, Lignocellulose, Integrated pretreatment, steam explosion, industrialization.

INTRODUCTION

Making the process cost-competitive is critical now for the industrialization of lignocellulose refining. Researchers have mainly concentrated on ethanol production from cellulose which only accounts for 30% of lignocellulose. However, about 70% lignocellulose including lignin and hemicelluloses are wasted. So, no matter how high the yield of enzymatic hydrolysis is, the cost of raw material is all apportioned to single product, leading to its high price. Therefore, we propose the concept of fractional conversions (Chen and Qiu, 2010) that fractionates lignocelluloses into different fractions suitable for various products, leaving almost no residues (Chen and Qiu, 2010). So the cost of raw materials and refining process are apportioned to multiple products. However, during long time evolution process, lignin content in three tissues increases: vascular tissue to transport water, sclerenchyma tissue to support stem and epidermic tissue to avoid moisture evaporation. Moreover, cellulose connects lignin and hemicellulose with hydrogen bond, and hemicellulose combines lignin with covalent bond. So, cell wall with complex structure is recalcitrant to enzymatic hydrolysis and other physical or chemical effects. If separating cellulose, hemicelluloses and lignin completely and subsequently hydrolyzing big molecule into chemicals, it would involve high solvent and energy, not to mention synthesizing other products from chemicals. This process is contrary to the principle of energy utilization, leading to high cost. So we design the process of selective deconstruction for fractional conversion. By this way, structure characteristics would be considered and applied while converting lignocellulose to biofuel, biomaterial or biochemical. And economic feasibility for lignocellulose industrialization would be improved with the principle multiproducts orientation. To obtain multiple products with selective deconstruction, single pretreatment method could hardly fulfill the requirements (Agbor et al., 2011). So we establish

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integrated pretreatment technologies to make the advantages of each pretreatment technology complementary, bringing to multiple products through selective deconstruction.

This paper highlights the mechanism to integrate various pretreatment technologies based on the analysis of the heterogeneity of lignocellulose. Moreover, research advances are presented and industrial demonstration is provided.

INEVITABILITY OF INTEGRATED PRETREATMENT FOR LIGNOCELLULOSE

Pretreatment method for lignocellulose

The reason to use lignocellulose in the early time was to complement the shortage of food and fuel owing to congestion of population in many developing countries (Klyosov, 1986). Lignocellulose was mainly applied by three kinds of methods. The first kinds focused on single product with single pretreatment technology before 1990 (Kawamori et al., 1986; Taniguchi et al., 1982a; Zadra il, 1977; Wayman and Parekh, 1988). And then integrated pretreatment technology appeared for single product (Carrasco and Roy, 1992; Maekawa, 1996; Holtzapple et al., 1991) also. In the 21 century, human began to care about the problems of environment, energy and rural development. So, integrated pretreatment for multiproducts was developed in order to find the alternative of petroleum. However, back in 1987 (Klyosov, 1986), COALBAR Company in Brail had used lignocellulose for both ethanol and charcoal. So the division time above is not so strict, but research focuses are different in different stages.

Single pretreatment technology for single product

Before 1990, lignocellulose was only converted to ethanol with single pretreatment technology including chemical, physical and biological methods.

Chemical methods referred to dilute acid or alkali (Kawamori et al., 1986), ozone (Bono et al., 1985), zinc chloride (Cao et al., 1995). Dilute acid included dilute sulfuric acid; dilute hydrochloric acid, hypochlorite (David and Atarhouch, 1987), peracetic acid (Taniguchi et al., 1982b), sulfur dioxide (Wayman and Parekh, 1988). There were also single pretreatment nowadays for single product, such as fumaric acid, maleic (Kootstra et al., 2009) and ionic liquid (Liu and Chen, 2006). All the researches above were aimed to improve enzyme hydrolysis rate. And phosphoric acid was also applied to improve lignocellulose edibility (Deschamps et al., 1996). Physical pretreatment technology included mechanical comminution, steam explosion (Grous et al., 1986), hot water (van Walsum et al., 1996), gamma-ray (Bono et al., 1985), microwave (Ooshima et al., 1984), organic solvent (Lipinsky and Kresovich, 1982), ammonia freeze explosion (Holtzapple et al., 1991). With the hot water pretreatment, two stages hydrolysis at high temperature was applied to avoid the effect of furfural (Torget and Teh-An, 1994). Biological method was mainly used to hydrolyze lignin with microorganism (Hatakka, 1983), reducing inefficacious absorption and enhancing enzyme hydrolysis rate. And microorganism pretreatment was also researched to produce single cell protein (Taniguchi et al., 1982a) and feed (Zadra il, 1977).

Industrial application about single pretreatment for single product was backed to 1913 (Klyosov, 1986). In Georgetown, South Carolina, pin mill waste was pretreated with 2% sulfuric acid at 175°C in rotary steam heated digesters, producing 5000 gallon ethanol per day. Subsequently, a second plant was built in Fullerton, Louisiana. However, both plants became profitable until the middle 1920s because of extremely low cost sawdust waste and the lack of environmental controls. So, lignocellulose conversion into single product with single pretreatment method could hardly industrialize nowadays because of high feedstock price and strong environmental consciousness.

Integrated pretreatment for single product

As early as 1986 (Klyosov, 1986), steam explosion pretreatment was pointed out to be one of the most economical and effective technology. Pretreatment methods integrated with steam explosion included methanol, peroxide hydrogen, sodium hydroxide (Maekawa, 1996) and ammonia (Carrasco, 1992). Moreover, in order to enhance biogas production in anaerobic digestion, corn stover was pretreated with sodium hydroxide integrated with green oxygen or 1,4-dihydroxy anthraquinone (Ping et al., 2010), and rice straw was pretreated with grinding integrated with calcium hydroxide (Cui et al., 2011).

To prepare fiber, ultrasonic integrated chemical pretreatment was applied for poplar. During chemical pretreatment, there were two processes including delignification with sodium hypochlorite and removal of gel as well as hemicelluloses with sodium hydroxide (Chen et al., 2011b). Though the price of petroleum is rising and environmental consciousness is becoming stronger and stronger, technology to produce ethanol or biogas still lacks of competitiveness because of low yield. So, how to convert all components into products is a key step to reduce cost.

The inevitability of integrated pretreatment for multiproduct

During forty years after the Second World War, only one biofuel company in Soviet Union succeeded as a commercial operation. The essential reason was that lignocellulose was considered as multifunctional raw material and converted into not only ethanol (cellulose) but also yeast, furfural (hemicellulose) and fuel (lignin). Up to 1986, this company consisted of 40 full-scale plants with a maximum capacity of 1000 tons of wood material per plant per day. The production from this technology was 1.5 million tons of fodder yeasts and 195 million L of ethanol. It proved that integrated pretreatment for multiproduct was the only way for the industrialization of lignocellulose refining.

As early as 1986 (Klyosov, 1986), integrated pretreatment for multiproduct was proposed as an effective way to apply lignocellulose which was considered as wastes of large number then. In 1993 (Wyman and Goodman, 1993), economic model revealed that multiproduct from lignocellulose could decrease cost of each product. However, effective pretreatment method had not reported.

It is an inevitable direction that bioproducts become alternative of those made from petroleum. However, lignocellulose refining technology could hardly been industrialized due to the lack of competitiveness, though related technology has been researched as long as 100 years and the price of petroleum has been rising nowadays. Related researches mainly focused on biofuels, but in the long term, lignocellulose would be the only raw materials for chemicals when petroleum is running out. Therefore, the importance of biochemicals should not be ignored. Even biochemicals could not take place of those from petroleum, multiproduct can make the industrialization of lignocelluloses refining beneficial.

DESIGN OF INTEGRATED PRETREATMENT FOR LIGNOCELLULOSE

Connotation of integrated pretreatment for lignocellulose

Integrated pretreatment is the integration of two or more physical, chemical and biological pretreatments instead of their simple combination. It is conceived according to the heterogeneity of lignocellulose, abiding by the principle of selective deconstruction and fractional conversion, obtaining economic, steady and environment friendly products.

According to the heterogeneity of lignocellulose

It has been found that the component and structure are heterogeneous for different kinds of lignocelluose such as corn stover, wheat straw and rice straw, and for different organ, tissue and cell from the same kind.

1. For different feedstock, components and structure are obviously different.
2. For different organs from the same feedstock, such as leaf, sheath, rind, pith and so on, components and structure are different because the percentage of various tissues are different, resulting in diversity of enzyme hydrolysis of different organs (Chen et al., 2011a).
3. The component and structure of different tissue are different. According to the classifying method proposed by Sachs (1875), the mature tissues of plant are classified as dermal tissue system, vascular tissue system and ground tissue system. The dermal tissue system includes epidermis and periderm. Vascular tissue system is composed of xylem and phloem. Ground tissue system consists of parenchyma (including secretory), collenchymas and sclerenchyma.

The surface of dermal tissue system often contains cuticle. Cuticle consists of cutin and wax, and cutin is polymer of C_{16} and C_{18}. The parenchyma under epidermis is hardened, leading to high lignin content. Vessel wall is secondary thickened and lignified, so, lignin content is high. However, in phloem, sieve tube mainly consists of primary wall. In the ground tissue system, cell wall of parenchyma is lightly lignified but sclerenchyma contains secondary wall which is high in lignin.

4. The component and structure of the different cell are different. As presented above, component of different cell in the same tissue is also different. There is also some specialized cell, such as silica cell which is located in the middle of long cell around vein. The wall of silica cell is silicidized.
5. The heterogeneity of different component is mainly demonstrated in lignin and hemicellulose. Phenylpropane is the basic framework of lignin mainly including syringyl, guaiacyl and hydroxy-phenyl. The heterogeneity of lignin from different cell, tissue or organ is caused by variations in the polymer composition, size, cross-linking and functional groups (Bonini et al., 2008).

Structure units of hemicellulose include D-xylose, D-glucose, D-galactose, D-allose, 4-O-methyl-D-glucuronic acid, D-galacturonic acid and D- glucuronic acid. There is also less L-rhamnose, L-fucose and other neutral sugar with methoxy and acetyl. Heterogeneous polysaccharide in Hemicellulose consists of 2 to 4 structure units above.

Therefore, conversion technology for these raw materials should be established on the basis of the heterogeneity in different levels. For example, vascular tissue is high in lignin, so it is suitable for lignin extraction instead of ethanol preparation. But for ground tissue system, especially parenchyma is easy to be hydrolyzed by cellulase because of high cellulose content.

Comply with principle of selective deconstruction and fractional conversion

Selective deconstruction means two aspects. On one hand, considering from raw materials, integrated pretreatment should be based on the heterogeneous property of raw materials instead of separating cellulose, hemicelluloses and lignin completely. On the other hand, considering from products, integrated pretreatment should be based on the requirements of products to make best of functional components or structure. That is to convert directly with selective deconstruction, avoiding hydrolyzing into small molecules to reduce energy consumption.

For example, ethanol from polysaccharide, especially cellulose is essential to obtain a long-term sustainable supply of energy. Cellulose content is high in parenchyma tissue and phloem which are suitable for enzyme hydrolysis. However, epidermal tissue, xylem and sclerenchyma, especially vessel in xylem are high in lignin. As the raw materials for ethanol production, high cellulose content and less lignin content are required. So parenchyma and phloem should be obtained and then hydrolyzed directly without further lignin removal. The residual epidermal tissue, xylem and sclerenchyma, which are high in lignin, can be converted into board or further refined for lignin product.

Fractional conversion means to produce mainly one or two products as well as other by-products based on the principle of eco-industry. Multiproduct got from fractional conversion includes biofuel, biomaterials and biochemicals. Biofuel includes ethanol, butanol, bio-oil, hydrogen, biogas and feedstock for power generation. Biomaterials include not only board and phenolic resin from lignin but also biomass composite materials made by adding other polymer, metal or inorganic salts. Biochemicals are products from lignocellulose with the conversion technology of thermochemistry or biochemistry.

Compared with single product, multiple products would apportion the cost of raw material and other consumption to reduce to cost of each product. For example, if the price of corn stover was 93.78$/t, ethanol would be only apportioned one third (31.26$) because ethanol is made from cellulose which accounts for about one third of corn stover. And other 62.52$ is apportioned to products of lignin (for example, phenolic resin) and hemicelluloses (for example, butanol and acetone).

Complementary integration of different pretreatment technologies

Complementary integration is to make different pretreatment technologies complementary, obtaining multiproduct with one or two main products.

Usually, in order to obtain one product with high yield, several pretreatment technologies are involved, which is lack of competitiveness because of high cost and large wastes. Complementary integration highlights multiple-product orientation to reduce the cost and remove wastes. By this way, different components including cellulose, hemicellulose, lignin, even ash are converted into final products almost without wastes.

Take steam explosion for example, hemicellulose is hydrolyzed by auto catalyzing effect at high temperature. And then hydrolysates could be washed out and converted into biogas or butanol through fermentation. However, lignin could not be separated by steam explosion.

Lignin could be dissolved by alkali. Therefore, steam explosion and alkali extraction technologies could be integrated to separated selectively hemicellulose, lignin and cellulose. Meantime, the strength of steam explosion reduces without the aim to separate lignin. And alkali used is less after steam explosion pretreatment because the tight structure of lignocellulose is destroyed. By this way, hydrolysate of hemicelluloses, cellulose and lignin could be converted into different products.

Advantages of integrated pretreatment for lignocellulose

Compared with single pretreatment technology, the advantages of integrated pretreatment for lignocellulose are as follows.

1. Integrated pretreatment is oriented by multiproduct to make best of each component for different products. Therefore, the economic value of lignocellulose increases and discharge reduces.
2. Integrated pretreatment is based on the heterogeneity of lignocellulose in different levels, especially on cell level. For example, cells of vessel and parenchyma could be separated by steam explosion integrated mechanical carding (Chen and Fu, 2012), which is regarded as selective separation. And the vessel, which is high in lignin, could be used for spinning, pulping and board. Meanwhile, parenchyma cell and phloem cell which are rich of cellulose could be converted into biofuels by enzymatic hydrolysis and fermentaion.
3. Integrated pretreatment is of wide adaptability because there are more parameters could be adjusted. Therefore, integrated pretreatment is also flexible and fit for various raw materials from different regions and planting manners.
4. According to the property of lignocellulose in terms of components and structure, many ideas and technologies could be integrated including those from paper making, pinning and board industry, especially petroleum refining which should be rational, economic, effective, clear and operable. For example, the idea of petroleum refining could be used in lignocellulose conversion to separate selectively for different products.
5. Integrated pretreatment makes different technologies complementary in advantages. By this way, the strength of each technology is reduced, leading to law pretreatment cost.

STATUS OF INTEGRATED PRETREATMENT FOR LIGNOCELLULOSE

As discussed previously, integrated pretreatment is to integrate pretreatment technologies to make best of the advantages of each single technology. That means to make best of one pretreatment method as well as to create advantages for next pretreatment methods. Steam explosion has been regarded as one potential pretreatment technology (Grous et al., 1986; Guo et al., 2011) and applied for various products from lignocelluloses (Biswas et al., 2011; Brugnago et al., 2011; Jacquet et al., 2011; Li et al., 2009; Rocha et al., 2012; Zimbardi et al., 2009). At present, integrated pretreatment oriented by multiproduct is mainly about steam explosion integrated pretreatment. The authors Zhang and Chen (2012), Chen and Liu (2007), Jin and Chen (2006) and Xu et al. (2001) have summarized advantages of steam explosion from decades of research and industrialization of steam explosion technology as follows:

1. Steam explosion hydrolyzes most hemicellulose, reducing the complexity of cell wall component (Chen and Qiu 2010).
2. At the instant of steam explosion, steam in and among the cells spurts out, destroying cell wall and the connection of tissue. As a result, the tight structure of tissue and cell wall is loosened. Plus the hydrolysis of hemicellulose, porous structure of lignocellulose is formed after steam explosion. Therefore, specific surface area increases, which could enhance mass transfer rate and improve the accessibility ((Zhang and Chen 2012).
3. Purity of products is enhanced after separating hydrolysate of hemicellulose and lignin, as well as other water soluble components (Peng and Chen, 2012).
4. Steam explosion pretreatment is clear, effective, efficient and none chemical additives (Chen and Qiu 2010).
5. Steam explosion is easy to operate and spread.

Therefore, lignocellulose after steam explosion is suitable for further physical, chemical and biological pretreatment, which is the very reason for steam explosion to become research focus. Meantime, steam explosion integrated pretreatment explains the connotation of integrated pretreatment technology in this paper.

Steam explosion-washing-solvent extraction-Bauer screening integrated pretreatment (SE-W-S-BS)

Acetyl attached in hemicellulose is hydrolyzed during steam explosion and become acetic acid. Then, acetic acid catalyzes the degradation of hemicellulose at high temperature. Monosaccharide from hemicellulose is water soluble. Therefore, hydrolysates from hemicelluloses could be washed out first and then converted into final product. After steam explosion, lignin is more soluble in ethanol and glycerin because phenolic hydroxyl buried in lignin is exposed out. To obtain hemicelluloses and lignin fractions, washing and solvent extraction has been applied after steam explosion. It was revealed that (Chen and Liu, 2007) hemicellulose recovery yield reached 80% by washing steam exploded wheat straw with water for four times.

The solution obtained from washing mainly contained xylose. The residual solid after washing was extracted by ethanol. Ethanol was distilled then at low temperature and the recovery yield reached 88.04%. The extraction liquid after distilling was glue. Lignin in the glue could be precipitated by adding 0.3 mol/L hydrochloric acid. And the precipitated lignin was purified later with recovery yield of 75%. Enzymatic hydrolysis test revealed that, after extraction, reduced sugar yield reached 31.41% which was 5.13 times higher than that of grinding wheat straw.By comparison to methanoic acid, propionic acid, ethylene glycol, butanediol, glycerin was the best one to extract lignin. Cellulose of wheat straw was reserved by 92% (Sun and Chen, 2008) and the yield of enzymatic hydrolysis reached 54% after steam explosion-washing-glycerin extraction integrated pretreatment.

The enzymatic hydrolysis yield of cellulose was also low after steam explosion-washing-solvent extraction pretreatment because of lignin residuals. In plant tissue, cells which are high in lignin are longer including cells from epidermis tissue, sclerenchyma and vessel tissue. However, cells which are low in lignin are shorter such as parenchyma cells. Short cells would be fit for enzymatic hydrolysis if they could be separated from long cells. So, Bauer screening pretreatment was applied.Two grades were obtained after Bauer screening. Scanning electronic microscope analysis showed that grade 1 was mainly fiber tissue cell (from epidemic tissue and mechanical tissue) and grade 2 was mainly miscellaneous cell (non-fiber tissue cell) with percentage of 47.6% and 19.9% respectively.

The average length and width of the long fiber were 1.067 mm and 13.893 μm which was similar to that reported (1.39 mm and 13.0 μm) in Papermaking Raw Materials of China an Atlas of Micrographs and the Characteristics of Fibers. The ratio of length to width was 76.81, which was among that of conifer and broadleaf but higher than the requirement of paper making materials (Fang and Liu, 1996).Steam explosion -Bauer screening integrated pretreatment was also used for corn stover. It revealed that product smaller than 75 μm was easier to be hydrolyzed by cellulase than the product bigger than 600 μm. Therefore, process was designed to produce the main product of butanol as shown in Figure 1.

Steam explosion-washing-alkali extraction-mechanical carding integrated pretreatment (SE-W-A-MC)

Though hydrolyzed lignin was extracted by steam explosion integrated solvent extraction pretreatment, lignin

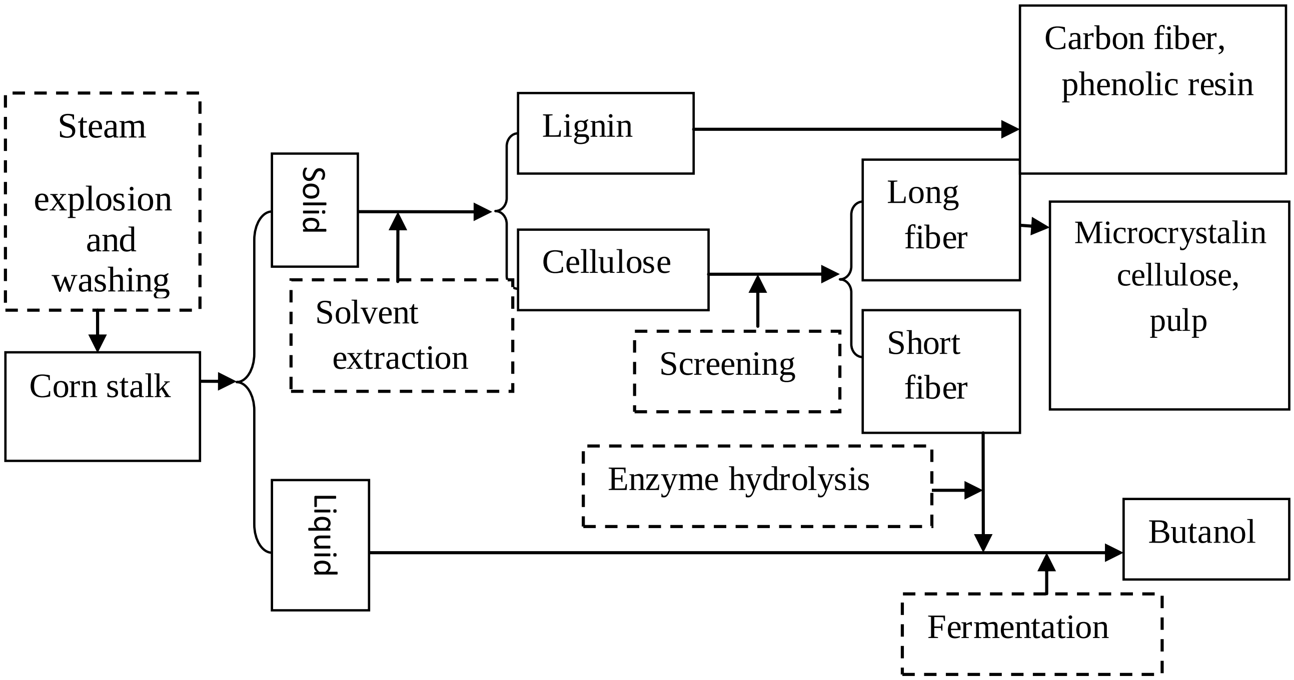

Figure 1. Flow chart of steam explosion-washing-solvent extraction-Bauer screening integrated pretreatment for corn stalk with the main product of butanol.

lignin residuals was also recalcitrant to cellulase. Moreover, lignin residuals were inhibitor in fermentation for butanol. So, methods were further explored to hydrolyze lignin.

Research revealed that lignin could be separated by alkali oxygenation. Wang and Chen (2011) and Cara et al. (2006) also reported that lignin in lignocellulose could be removed by pretreatment to improve the yield of enzymatic hydrolysis and fermentation property. Tissues consist of different cells and components could be fractionated by mechanical carding equipment (Chen and Fu, 2012). To enhance the yield of lignin, enzymatic hydrolysis and fermentation, steam explosion-washing-alkali extraction-mechanical carding integrated pretreatment was researched.

With this process, the recovery yields of cellulose and lignin reach 70 and 80%, respectively.

Normally, for butanol fermentation, sugar concentration in culture medium should be lower than 60 g/L. The total sugar content was 45.24 g/L in the enzyme hydrolysate of corn stover pretreated with steam explosion combined 1% NaOH+4% H_2O_2 (Wang and Chen, 2011). So, hydrolysate from enzymatic hydrolysis could satisfy the requirements for butanol fermentation. Further research revealed that soluble lignin content in enzyme hydrolysis was 1.2 g/L which would not inhibit butanol fermentation. As a result, the total solvent content was 12.10 g/L with the yield of 0.27 and productivity of 0.17 g/(L·h).

Therefore, process was designed with butanol as main product (Figure 2).

Steam explosion integrated super grinding pretreatment (SE-SG)

Superfine-grinding has been applied widely in the chemical industry, and its energy consumption is not as high as traditional grinding methods (Yang, 1988).

Therefore, superfine-grinding technology is considered to be imported into steam explosion integrated pretreatment to satisfy lignocellulose conversion requirements (Jin and Chen, 2006). Water-holding capacity and toughness is different between fiber tissue and non-fiber tissue including ground tissue and epidemic tissue (Yang, 2001), leading to different grinding property.

Therefore, steam explosion integrated wet grinding pretreatment was studied by taking rice straw as material.Fiber part accounted for 70.4% of dry weight after steam explosion integrated wet grinding pretreatment (Jin and Chen, 2006). In the fiber part, fiber cell accounted for 63.1% which was higher than that of raw rice straw by 37.8%. Fiber component accounted for 65.6% in fiber part which was higher than that of raw rice straw by 74.9%, and the ground tissue cell accounted for 33.5%.

This indicated that steam explosion-wet superfine grinding pretreatment could separate fiber cell as well as fiber component to some extent.

Enzymatic hydrolysis test revealed that hydrolysis rate and reducd sugar yield of fiber tissue part was the highest compared with that of raw rice straw and steam exploded rice straw. Especially, reduced sugar yield was

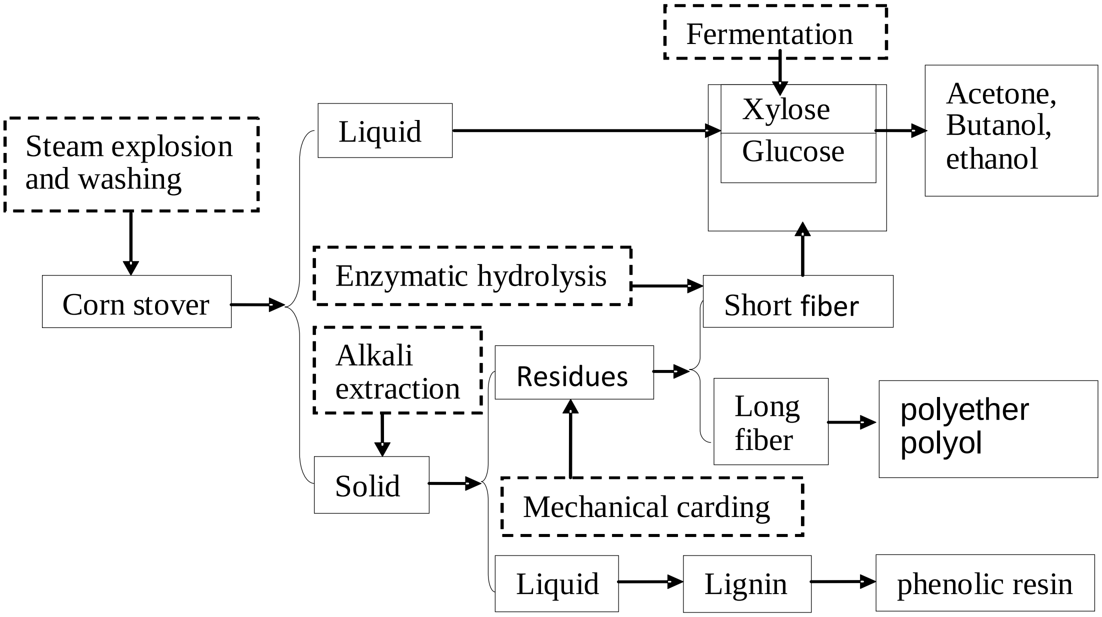

Figure 2. Flow chart of steam explosion-washing-alkali extraction-mechanical carding integrated pretreatment for corn stover with butanol as main product.

higher than that of raw rice straw by 60.0%. Therefore, fiber tissue separated by steam explosion combined wet superfine grinding was suitable as enzymatic hydrolysis material.

Simultaneous saccharification and fermentation test showed that ethanol yield of fiber tissue part pretreated by steam explosion integrated wet superfine grinding method reached 8.6%, but that of steam exploded rice straw and raw rice straw were 7.3% and 6.7%, respectively after 48 h fermentation. Therefore, steam explosion combined wet superfine grinding pretreatment increases the ethanol yield as well as its productivity.

Other combined pretreatment waiting for integrating steam explosion combined ionic liquid pretreatment (SE-IL)

Compared with the organic solvent and electrolyte, there are some advantages for ionic liquid and it is regarded as one of the three green solvents including supercritical carbon dioxide, aqueous two-phase and ionic liquid. At first, it is nearly no steam pressure, so, the pollution problem of other volatile organic solvent is avoided. Then, it is chemically and physically stable among broad range temperature adjustability (from lower than 25 to 300°C) and electrochemical window. Finally, it can be adjusted by the design of cation and anion, so the solubility to inorganics, organics and water is changed and its acidity can be adjusted to super acid.

Previous experiment (Liu and Chen, 2006) showed that the contents of cellulose, hemicellulose and lignin of wheat straw decreased after steam explosion combined ionic liquid pretreatment. The ionic liquid was self-prepared. To protect cellulose, acid or alkali was inputted into ionic liquid. It was revealed that sodium hydroxide could improve solubility and protect cellulose. However, 1% sulfuric acid reduced the content of hemicellulose and cellulose, but improved the lignin content. Further research showed that, enzymatic hydrolysis of wheat straw reached 102.49% (the hydrolysate of hemicelluloses was included) after steam explosion combined ionic liquid pretreatment.

Steam explosion combined laccase pretreatment (SE-L)

Lignin-carbohydrate complex (LCC) inhibits enzymatic hydrolysis. So it is important to separate LCC before hydrolysis. Enzyme pretreatment is mild and specific. Therefore, steam explosion combined enzyme pretreatment was researched to remove LCC (Qiu and Chen, 2012). The enzyme used included laccase and feruloyl esterase or xylanase. Steam exploded material was pressed by screwing to separate the solid and liquid. And then, enzyme combination was input into the solid part. When laccase and feruloyl esterase were used, the yield of cellulose, hemicellulose and lignin hydrolysis of corn stover were 5.65%, 10.97% and 33.93%, respectively compared with the content of steam explosion corn stover. Hydrolysis products of lignin and hemicellulose could be converted to other products of high value. This pretreatment was high-rate, efficient,mild and specificity.

Moreover, water wastage was decreased by screwing press instead of washing. Importantly, the increased hydrolysis rate could provide subtract with high sugar content for subsequent fermentation.

Steam explosion combined electricity catalyzing pretreatment (SE-EC)

Electricity catalyzing is being applied in waste water pretreatment because it is without chemical reagent and second pollution, and easy to operate. Pulp could be bleached by redox effect of electricity catalyzing. Redox effect catalyzes lignin to destroy its structure, consequently, lignin is removed and pulp is bleached (Ma et al., 2003).

Therefore, steam explosion combined electricity catalyzing pretreatment was researched (Ding, 2010). With this pretreatment, hemicellulose was hydrolyzed in steam explosion process and lignin was degraded in electricity catalyzing process. As a result, hemicellulose, lignin and cellulose were separated and could be converted into high value products separately.

Compared with that of steam exploded corn stover, the contents of lignin of core straw pretreated by steam explosion combined electricity catalyzing at the voltage 1.5, 2.5, and 5 decreased 6.9 12.7 and 20.0%, respectively. And the content of cellulose was reduced 1.0 2.8 and 4.3%. The content of hemicellulose decreased 10.1, 14.6 and 16.9%. However the soluble content increased 50.0, 84.2 and 111.8% respectively at voltage 1.5, 2.5 and 5 V. This revealed that electricity catalyzing pretreatment degraded lignin as well as hemicellulose and cellulose, leading to soluble component improvement. Glucose content in corn stover hydrolysate increased by 25.4% at the voltage 1.5 V after steam explosion combined electricity catalyzing pretreatment.

Steam explosion combined photochemistry pretreatment (SE-P)

Steam explosion combined photochemistry pretreatment was researched (Bonini et al., 2008) to convert lignin into by product of pulp and bleaching process. Pine and corn stover were impregnated in dilute acid, steam exploded and washed by hot water firstly. Then, lignin was extracted by 1.5% sodium hydroxide solution and precipitated at pH 2 with 20% H_2SO_4. Lignin from pine was put into a tube and saturated with bubbling oxygen for 1 h, and the irradiation was performed by using a 50 W tungsten-halogen lamp. Lignin from corn was dissolved in 1:1 acetonitrile-methanol (20 ml) and flushed with ozone generated by using Ozone Generator 500 M. Characterization with NMR revealed that ozonolysis of steam exploded lignin did not recovery fine chemicals with the exception of oxalic acid. This was caused by acid impregnation which made lignin destroyed. And an initial polymerization process was observed, which was induced by the formation of radicals in lignin components obtained from steam explosion pine. It was found that steam explosion was a method affording the highest destroying of corn stover lignin, making lignin easily oxidized by ozone.

Steam explosion combined acid pretreatment (SE-A)

Dilute-acid can make hemicelluloses soluble, therefore it has been widely applied in lignocellulose pretreatment. It was found (Chen et al., 2011b) that rice straw pretreated by dilute-acid/steam explosion had a higher xylose yield, a lower level of inhibitor in hydrolysate and a greater degree of enzymatic hydrolysis, which resulted in a 1.5-fold increase in the overall sugar yield while compared to acid-catalyzed steam explosion.

Alexandre Emmel (Emmel et al., 2003) investigated steam explosion of Eucalyptus grandis under various pretreatment conditions (200 to 210°C, 2 to 5 min) after impregnation of the wood chips with 0.087% and 0.175% (w/w) H_2SO_4. It was found that the yield of alkali-soluble lignin increased with higher acid impregnation at high pretreatment temperature.

Non-cellulosic constituents such as hemicelluloses and lignin were removed by steam explosion combined bleaching or acid treatments (Deepa et al., 2011). And fiber diameter reduced after steam explosion followed by acid treatments. Percentage yield and aspect ratio of nanofiber obtained by this technique was found to be higher than other conventional methods.

Comparison of different integrated pretreatment

Steam explosion integrated pretreatment technologies are compared in terms of recovery yield, purity of fractions, cost-competitiveness and environment-friendliness (Table 1). It shows that SE-W-A-MC is both cost-competitive and environment-friendly because there is no chemical additions and easy to operate. Compared with that of SE-W-S-BS, the purity of fractions is enhanced by the process of SE-W-A-M. SE-SG, SE-EC, SE-P require pretreatment of raw materials, so they are not cost-competitive. For SE-IL and SE-L, the cost of ion liquid and laccase is high. And it is obvious that SE-A involves chemical additions which are not acceptable for environment.

DEMONSTRATION OF STEAM EXPLOSION INTEGRATED PRETREATMENT FOR LIGNOCELLULOSE

Lignocellulose is heterogeneous, the same as its

Table 1. Comparison of different integrated pretreatment.

Pretreatment	Recovery yield (%)[a]	Purity of fractions (%)[b]	Cost-Competiveness[c]	Environment-friendliness[d]	Total[e]
SE-W-S-BS	70-85	75-85	Y	N	62.0-N
SE-W-A-MC	70-90	80-95	Y	Y	70.0-Y
SE-SG	85-95	80-90	N	Y	76.5-N
SE-IL	80-90	85-95	N	Y	76.5-N
SE-L	80-95	75-85	N	Y	72.0-N
SE-EC	80-95	70-85	N	Y	72.0-N
SE-P	80-90	70-85	N	N	68.0-N
SE-A	80-95	70-85	Y	N	70.0-N

SE, Steam explosion; W, washing; S, solvent extraction; BS, Bauer screening; A, alkali extraction; MC, mechanical carding; SG, super grinding; IL, ion liquid; L, laccase; EC, electricity catalyzing; P, photochemistry; A, acid. [a]Recovery yield means to the weight percentage of all fractions to total raw materials. [b]Purity of fractions means to the weight percentage of ideal fraction to actual fraction. [c]Cost includes equipment depreciation, additions, labor and power. [d]Environment-friendliness means that there is no chemical additions, no wastes left, less electricity and water consumption. [e]For total; it is calculated as follows: $Percentage(\%) = recovery\ yield \times purity\ of\ \ fraction$; $N \times N = N; N \times Y = N; Y \times N = N; Y \times Y = Y$.

conversion property. The authors have established three platforms for lignocelluloe refining including law pressure, non-pollution steam explosion platform (Zhang and Chen, 2012), solid-state enzymatic hydrolysis and solid-state fermentation platform, fermentation and separation coupling platform (Li and Chen, 2007). For each platform, pilot test apparatus have been designed, as well as industrial equipment. By process integration, straw refining systems of multi-layer have been established and industrialized in plant about lignocellulose ethanol, butanol, board, spinning and so on. Especially, in September, 2010, Laihe Chemcial Co., Lid. located in Jilin Province, China introduced SE-W-A-MC (Wang and Chen, 2011; Chen and Fu, 2012). Its capacity is 300 thousand tons corn stover annually.

The products from this technology were 50 thousand tons butanol, acetone and ethanol, 30 thousand tons pure lignin which could be converted into 20 thousand tons phenol formaldehyde resin adhesive, 120 thousand tons cellulose which could be converted into 50 thousand tons biological polyether polyol. The cost of solvent reduces more than 50% after cost apportioning by lignin and cellulose. Other lignocellulose refining plants which adopt integrated pretreatment are also on the way.

CONCLUSION AND PERSPECTIVES

Research and industrial demonstration above reveal that integrated pretreatment is an effective way to convert different components into multiproduct of high value through selective deconstruction. Reduced sugar from the process of enzymatic hydrolysis become cost-competitive though cost apportioning by other products. Moreover, little waste leaves by converting cellulose, hemicellulose, lignin and other components into relative products separately. To provide valid theory for the process engineering of lignocellulose refining, more understanding are needed about the properties of various lignocellulose materials, as well as changes of molecular structure resulted from different single pretreatment technologies. And then, mechanism to integrate different pretreatment technologies in this paper could be basic references for designing processes for other raw materials. Moreover, equipment for industrialization should be designed and relative theory for industrial scale-up should be established to overcome problems in application.

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