Research progress on biorefinery of lignocellulosic biomass

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Abstract. The basic concepts of biorefinery and several models of today's biorefinery chemical platforms are introduced. According to the different utilization types of cellulose, it is divided into biorefining based on pulp and paper and biorefining based on fuel ethanol. It is proposed that biomass component separation technology is the core of biorefinery. The application of eutectic solvents in biorefinery was introduced around the separation of components. It was pointed out that the application of eutectic solvents to biorefinery is promising.

1. Introduction
Coal, oil, natural gas, etc. provide abundant energy and chemicals for human life. However, as a non-renewable resource, fossil resources have many problems such as insufficient reserves and environmental pollution, and there is an urgent need for alternative resources. As the most abundant natural renewable resource on the earth, lignocellulosic biomass has the advantages of carbon neutrality and easy access, and has broad application prospects. However, the traditional technology of directly converting and utilizing biomass single components has certain disadvantages, such as serious waste of resources, low added value of products, and large environmental pollution [1]. If the full range of lignocellulose can be utilized and converted into high value-added, diversified products and energy sources, the goal of “biorefinery” can be achieved [2]. At present, the research hotspots of biorefinery mainly consist of biorefinery based on pulp and paper [3] and biorefinery oriented to bioethanol, but the core of both is based on component separation technology to make lignocellulosic biomass. The separated structure matches the conversion needs of downstream high value products. However, few people have combed the two types of biorefinery models. This paper reviews several common patterns of two types of biorefinery chemical platforms and the application of eutectic solvents in the separation and pretreatment of lignocellulosic biomass components, in order to provide a certain design for the biorefinery model guide.

2. Biorefinery based on pulp and paper
The pulping and papermaking process is an important part of the national industry. If it can realize the biorefinery of the whole component, it can greatly improve the national economic level. Many experts at home and abroad have used the SWOT analysis model to analyze the pulp and paper industry combined with biorefinery [4-5], and found the mature biomass power grid, pulp by-product market, and the natural scale of the pulp mill. Factors such as equipment and stable supply of wood raw materials make natural refining for pulp and paper industry a natural industrial advantage. However, the more severe delignification conditions in the pulp and paper process have limited their high value utilization. Therefore, the current research focuses on the design of biorefinery mode of a certain component. In
general, it can be divided into two categories: lignin-based biorefinery, hemicellulose-based biorefinery.

2.1 Lignin-based biorefinery

In China, the pulp and paper industry produces about 10 million tons of lignin per year, and most of it is drained with black liquor. If the lignin removed during these pulping processes is recovered, and the lignin is used for high value based on the structure of these lignin, it is the so-called biorefining of lignin, and most of them utilize the natural flavor of lignin. In the traditional process, the remaining lignin (such as kraft pulp lignin) is directly burned as an energy source or the lignin is sulfonated and directly modified to prepare a dispersant, a surfactant, a soil and water retaining agent, etc.\[^6\], but these are simple. The modification often fails to make full use of the structural characteristics of lignin, and the investment is huge but the income is not high.\[^7\]. Compared to the sulfonation of all lignin, it is better to use the pyrolysis/catalysis of lignin as the core of utilization to achieve a high natural level of "biorefinery."\[^8\].

Mortensen et al.\[^9\] proposed the production of commercial grade benzene compounds and fuels using the unique aromatic structure of lignin. The structure of lignin may undergo a large amount of condensation after the pulping process, so rapid thermal cracking is a promising high-value utilization method. Rapid pyrolysis is a method for preserving most of the energy in lignin in liquid product bio-oil under anaerobic conditions.\[^8\]. The heating rate is fast, and the lignin is rapidly decomposed into volatiles and condensed into High valued small molecule product. Further, the process parameters can be set according to different target products\[^10\]. For example, lignin pyrolyzed by a fixed bed reactor can obtain more guaiacol structure than a fluidized bed, which is very much for the conversion of water gas in the later stage. Favorable.\[^11\].

Gillet et al.\[^12\] first used Cu catalytic catalyzed depolymerization to simulate the beech and thatch lignin obtained by ethanol pulping method, and obtained a variety of high value-added products, such as eugenol, magnolol, caffeic acid and the like. These products have important applications in medicinal chemistry, as a precursor to platform compounds, etc., and lignin catalytic depolymerization is more economical than simply converting to fuel. At the same time, different structures of lignin will obtain different small molecular products after catalytic depolymerization, and the yields are also different. Therefore, the target product can also be obtained according to the control of production parameters. However, it appears that lignin catalytic depolymerization requires higher content of β-O-4 linkages in raw materials, and is not suitable for most pulping methods. The development of more efficient catalysts and how to improve the separation of lignin during pulping to inhibit structural polycondensation is a major challenge in the lignin catalytic mode.

2.2 Hemicellulose-based biorefinery

Hemicellulose-based biorefinery, which is often oriented to the production of dissolving pulp. In this route, the hemicellulose is first removed by a prehydrolysis method to obtain a residue. At this time, most of the linkages in the lignin carbohydrate complex have been broken, so that the amount of chemicals in the subsequent pulping process can be greatly reduced, and the damage to the original structure of lignin can be reduced, and the obtained lignin can be further advanced. Value utilization. On the other hand, in the pulp after removal of hemicellulose, cellulose of higher purity can be obtained. The reason for the production of dissolving pulp is that the pre-hydrolysis process will lead to a decrease in pulp production, which requires high economic value dissolving pulp for economic benefit compensation. The hemicellulose obtained by the prehydrolysis process can be further converted into high-valued products such as organic acids and furfural by biological/chemical treatment according to the structural difference.\[^13\]. However, the use of hemicellulose and lignin in this method still requires a broader idea to seek full use.

The solvent of the prehydrolysis method should generally meet four points: extract as much hemicellulose as possible; reduce the crystallinity of the cellulose as much as possible; avoid hemicellulose degradation as much as possible; and reduce the production cost as much as possible.\[^14\].
In terms of cost, the best solvent system is directly derived from the industry itself. Cabrera et al. \cite{15} found that paper green liquor can effectively extract hemicellulose from wood without affecting pulp quality. This method provides a new way of utilization for papermaking waste liquid, greatly reducing the cost, and its extract is rich in hemicellulose, which can be further used as a raw material for producing bioethanol. Water is the most widely used green solvent and is a good choice. The use of water as a solvent for prehydrolysis of hemicellulose has been widely used in Canada, and the Thurso pulp mill uses its extracted hemicellulose to convert to xylitol for biorefining \cite{16}. Further studies have found that the addition of some organic acids such as formic acid will greatly increase the hemicellulose content of water extraction, so acid-assisted hydrothermal pre-extraction of hemicellulose is a very promising method \cite{17}. Shandong Longli Group uses hydrothermal/dilute acid pretreatment to prepare dissolving pulp. The obtained oligosaccharide and high-purity lignosulfonate can be further used as feed processing or material use to realize biorefinery.

3. Biorefinery for fuel ethanol
Compared to the traditional pulp and paper industry, biorefining for fuel ethanol does not require a harsh delignification process. It is generally believed that the pretreatment process should remove hemicellulose as much as possible, and appropriately retain a part of lignin \cite{18}, so that the contact time of the enzyme with cellulose is longer while the cellulose accessibility is increased. This gentle treatment process makes the structure of the biomass component less destructive, and thus has more and wider utilization options in the subsequent high value process, which can also well balance the high cost in the pretreatment process. To better realize the economic benefits of biorefinery \cite{19}, this part mainly introduces from the perspective of raw materials: bio-refining based on hardwood raw materials and bio-refining based on grass raw materials.

3.1 Biorefinery based on hardwood raw materials
Biorefining based on hardwood raw materials is often based on the high value utilization of lignin. The extraction of biomass raw materials by alcohol solvent can easily obtain lignin with high purity and low molecular weight \cite{20}, and the residue has high enzymatic hydrolysis efficiency, and the alcohol solvent can be recycled and has high ecological value. However, how to use these lignin to balance the cost is still a problem that needs to be solved now. Wang et al \cite{21} pretreated eucalyptus with 2-propanol aqueous solution to separate lignin and residue. The delignification rate is 81.26% and the obtained lignin has a low molecular weight and a small structural change. The solid residue can be directly used for fermentation into bioethanol, and the enzymatic efficiency is significantly improved. Structural characterization revealed that the β-O-4, β-β and β-5 linkages gradually decreased as the reaction temperature increased and the reaction time increased. However, it seems that this method requires higher temperature and pressure, which makes it difficult to reduce the cost. Therefore, the high value utilization of lignin is the core of this method. The subsequent catalytic degradation of lignin may be its high value application direction.

3.2 Biorefinery based on grass raw materials
Since the grass raw material has a linkage bond such as ferulic acid ester, it is very easy to remove the lignin in the raw material, so that hemicellulose and lignin can be simultaneously utilized at a high level. After the biomass raw material is pretreated by the dilute acid/hydrothermal method, the degradation product of hemicellulose and the solid residue can be separated. The degradation product of hemicellulose is further processed into an oligosaccharide. The solid residue and then a one-step alkali treatment can separate the lignin and alkali treatment residue. The lignin obtained by the process has the unique structure, high purity and small molecular weight due to the particularity of the grass raw materials, and the alkali-treated residue rich in cellulose can obtain a high bioethanol yield after enzymatic saccharification. Sun et al \cite{21} studied the structural changes of biomass components in dilute acid coupled hydrothermal pretreatment and alkaline post-treatment with sweet sorghum stem as raw material. It was found that the rate of delignification was up to 79.3% after this treatment, and
good yields of oligosaccharides and bioethanol were obtained. The lignin β-O-4, β-β and β-5 obtained in the process were severely affected. Degradation becomes a small molecule. Relying on the wide application of the current dilute alkali grass lignin, this biorefinery model has been successfully commercialized and applied to Shandong Longli Group, and has achieved good economic benefits.

4. Eutectic solvents for biorefinery: prospects

The emergence of biorefinery has transformed more and more lignocellulosic biomass into other cellulose-based products such as bioethanol, and also produced more lignin and hemicellulose resources. Their separation and utilization efficiency affects the whole organism. Refining efficiency. Lignin is particularly important as a “natural anti-degradation barrier” [23]. However, the lignin in the traditional pulping and papermaking process undergoes a severe delignification process, and the structure changes greatly, which greatly limits its high value utilization. Therefore, it is necessary to find a component separation method to protect the original structure of lignin while efficiently removing lignin, which is the key to realizing biorefinery. The emergence of eutectic solvents offers a positive possibility for this goal.

The eutectic solvent was first proposed by Abbott et al. [24] and is characterized by non-toxicity, biodegradability, simple preparation, and low price. The essence is that strong hydrogen bonds are formed between the solids, thereby reducing the self-lattice to be liquid at room temperature. At present, eutectic solvents have been widely used in many fields.

The eutectic solvent is a type of solvent composed of a hydrogen bond donor and a hydrogen bond acceptor, so that the component of the eutectic solvent can be freely regulated to obtain a desired separation effect. Soares et al. [25] used dynamic light scattering to study the solubility of lignin monomer model compounds with industrial lignin (organic solvent and sulphate pulping) in several eutectic solvents. They found that the propionic acid/urea/water system dissolved 745.8 g/Kg of lignin under mild conditions at 40 °C, which has very efficient dissolution efficiency compared to conventional organic solvents. Alvarezvasco et al. [26] proposed that the mechanism of delignification is due to their ability to selectively break the ether bond between phenylpropane units in lignin. In addition to the separation of lignin, Morais et al. [27] also designed a highly efficient solvent for the selective dissolution of hemicellulose through structural regulation.

After pretreatment with eutectic solvent, lignocellulose forms a porous structure on the surface, which improves the enzymatic hydrolysis efficiency of cellulase. Xu et al. [28] pretreated corn stalks with choline chloride/formic acid and found that the fiber bundles became loose and small particles adhered to the surface, suspected to be residual hemicellulose and lignin complexes. After further enzymatic hydrolysis, the glucose yield is up to 99%, which greatly improves the efficiency of biorefinery. In addition, eutectic solvents can greatly improve the efficiency of conversion of xylose to 5-hydroxymethylfurfural [29]. It can be seen that the diversified structural design of eutectic solvents provides numerous potential opportunities for biorefinery. Will be great.

5. Conclusion

In the long run, biorefinery is one of the most important ways to maximize the utilization of forest biomass resources. Whether it is based on pulp or paper or bio-refining for fuel ethanol, the core is the requirement that the various components are separated to meet the downstream conversion products. Generally, for the application of the three major elements, it is more inclined to use its original structure to obtain greater economic benefits, which puts certain requirements on our component separation technology. Especially for the pulp industry, how to develop more efficient and gentle delignification technology to minimize the destruction of the original structure of lignin in the process is one of the key issues in today’s biorefinery. In addition, although the pretreatment technology for fuel ethanol has developed rapidly, there are not many practical industrial applications, and further efforts by forestry chemists are still needed.
References
[1] Wen, J. L., Yuan, T. Q., Sun, R. C. (2017) Biorefining and multistage utilization of lignocellulosic biomass, [J]. Biotechnology & Business (03): 94-99.
[2] Ragauskas A J, Beckham G T, Biddy M J, et al. (2014) Lignin Valorization: Improving Lignin Processing in the Biorefinery [J]. Science, 344(6185): 1246843-1246843.
[3] Heiningen A V. (2007) Converting a Kraft pulp mill into an integrated forest biorefinery [J]. World Pulp & Paper, 107(6): 38-43.
[4] Chambost V, Stuart A P. (2007) Selecting the most appropriate products for the forest biorefinery [J]. Industrial Biotechnology, 3(2): 112-119.
[5] Giurca A, Spath P. (2017) A forest-based bioeconomy for Germany? Strengths, weaknesses and policy options for lignocellulosic biorefineries [J]. Journal of Cleaner Production : 51-62.
[6] Tan, X. (2014) High value utilization of plant fiber lignin [J]. South China Agriculture, 8(21): 188-191+193.
[7] Xu, G. W. Ji, W. F., Wan, Y. H., Liu, C. Z. (2007) Energy Production with Light-Industry Biomass Process Residuals Rich in Cellulose [J]. Progress in Chemistry, (22): 1164-1176.
[8] Hu J, Zhang Q, Lee D, et al. (2018) Kraft lignin biorefinery: A perspective [J]. Bioresource Technology : 1181-1183.
[9] Mortensen P M, Grunwaldt J, Jensen P A, et al. (2011) A review of catalytic upgrading of bio-oil to engine fuels [J]. Applied Catalysis A-general, 407(1): 1-19.
[10] Fan L, Zhang Y, Liu S, et al. (2017) Bio-oil from fast pyrolysis of lignin: Effects of process and upgrading parameters [J]. Bioresource Technology : 1118-1126.
[11] Bu Q, Lei H, Wang L, et al. (2014) Bio-based phenols and fuel production from catalytic microwave pyrolysis of lignin by activated carbons [J]. Bioresource Technology: 142-147.
[12] Gillet S, Petitjean L, Agedo M, et al. (2017) Impact of lignin structure on oil production via hydropyrolysis with a copper-doped porous metal oxide catalyst [J]. Bioresource Technology: 216-226.
[13] Martin-Sampedro R, Eugenio M E, Moreno J A, et al. (2014) Integration of a Kraft pulping mill into a forest biorefinery: pre-extraction of hemicellulose by steam explosion versus steam treatment [J]. Bioresource Technology, 153(2): 236-244.
[14] Mussatto S I, Dragone G M. (2016) Biomass pretreatment, biorefineries and potential products for a bioeconomy development [J]. Biomass Fractionation Technologies for A Lignocellulosic Feedstock Based Biorefinery: 1-22.
[15] Cabrera M N, Arrosbide M F, Franzoni P, et al. (2016) Integrated forest biorefineries: green liquor extraction in eucalyptus wood prior to kraft pulping [J]. Biomass Conversion and Biorefinery, 6(4): 465-474.
[16] Li Z, Pan X. (2018) Strategies to modify physicochemical properties of hemicelluloses from biorefinery and paper industry for packaging material [J]. Reviews in Environmental Science and Biotechnology, 17(1): 47-69.
[17] Goldmann W M, Ahola J, Mikola M, et al. (2017) Formic acid aided hot water extraction of hemicellulose from European silver birch (Betula pendula) sawdust [J]. Bioresource Technology: 176-182.
[18] Zhang W, Sathitsuksanoh N, Barone J R, et al. (2016) Enhanced enzymatic saccharification of pretreated biomass using glycerol thermal processing (GTP) [J]. Bioresource Technology: 148-154.
[19] Wyman C E, Dale B E, Elander R T, et al. (2005) Coordinated development of leading biomass pretreatment technologies [J]. Bioresource Technology, 96(18): 1959-1966.
[20] Ferrini P, Rinaldi R. (2014) Catalytic Biorefining of Plant Biomass to Non-Pyrolytic Lignin Bio-Oil and Carbohydrates through Hydrogen Transfer Reactions [J]. Angewandte Chemie, 53(33): 8634-8639.
[21] Wang B, Shen X, Wen J, et al. (2017) Evaluation of organosolv pretreatment on the structural characteristics of lignin polymers and follow-up enzymatic hydrolysis of the substrates from
Eucalyptus wood[J]. International Journal of Biological Macromolecules: 447-459.

[22] Sun S, Wen J, Ma M, et al.(2014)Structural Elucidation of Sorghum Lignins from an Integrated Biorefinery Process Based on Hydrothermal and Alkaline Treatments[J]. Journal of Agricultural and Food Chemistry, 62(32): 8120-8128.

[23] Calvaruso G, Clough M T, Rechulski M D, et al.(2017)On the Meaning and Origins of Lignin Recalcitrance: A Critical Analysis of the Catalytic Upgrading of Lignins Obtained from Mechanocatalytic Biorefining and Organosolv Pulping[J]. Chemcatchem, 9(14): 2691-2700.

[24] Abbott A P, Capper G, Davies D L, et al.(2003)Novel solvent properties of choline chloride/urea mixtures[J]. Chemical Communications: 70-71.

[25] Soares B, Tavares D J, Amaral J L, et al.(2017)Enhanced Solubility of Lignin Monomeric Model Compounds and Technical Lignins in Aqueous Solutions of Deep Eutectic Solvents[J]. ACS Sustainable Chemistry & Engineering, 5(5): 4056-4065.

[26] Alvarezvasco C, Ma R, Quintero M, et al.(2016)Unique low-molecular-weight lignin with high purity extracted from wood by deep eutectic solvents (DES): a source of lignin for valorization[J]. Green Chemistry, 18(19): 5133-5141.

[27] Morais E S, Mendonca P V, Coelho J F, et al.(2018)Deep Eutectic Solvent Aqueous Solutions as Efficient Media for the Solubilization of Hardwood Xylans[J]. Chemsuschem, 11(4): 753-762.

[28] Xu G, Ding J, Han R, et al.(2016)Enhancing cellulose accessibility of corn stover by deep eutectic solvent pretreatment for butanol fermentation[J]. Bioresource Technology: 364-369.

[29] Assanosi A, Farah M M, Wood J, et al.(2014)A facile acidic choline chloride–p-TSA DES-catalysed dehydration of fructose to 5-hydroxymethylfurfural[J]. RSC Advances, 4(74): 39359-39364.