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The Application and Research Progress of Ionic Liquid in Biomass Transformation

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Abstract: As a new class of green solvent, ionic liquid has the properties of dissolving cellulose, lignin and biomass material, It is a very important material in the separation and conversion of biomass components. In the case of less and less oil, natural gas and other fossil energy, it has become urgent to accelerate the development and utilization of new green energy, and biomass, as a renewable resource, can not only effectively alleviate the energy tension in China, but also be very friendly to the ecological environment. However, because the existing biomass conversion technology is backward and relatively inefficient, which largely affects the development and utilization of biomass resources, this paper discusses the specific application and research direction of ion liquid on the concept of ion liquid in biomass transformation.

1. Introduction

Biomass mainly refers to organic substances that can be recycled and recycled, as common as crop straw, tree branches and plant residues. In today's industrial era, people's mining and utilization of fossil energy is gradually increasing, while the research on biomass resources is relatively little. With the less and less stock of fossil energy and its increasing damage to the global ecological environment, the development of biomass energy sources has been put on the agenda again. The main components of biomass are cellulose, hemicellulose as well as lignin, as a renewable resource, biomass can also be used to synthesize a range of chemical products and fuels. However, in the traditional biomass conversion production, strong acid or strong alkali are often used as a catalyst, which is not only easy to cause environmental pollution, but also the production is higher for equipment, which is not convenient for large-scale production. Ionic liquid has the advantages of strong stability and green environmental protection, and it is an ideal biomass catalyst. The catalytic and transformation role of ionic liquid in cellulose and lignin is studied, which is expected to provide some theoretical basis for promoting biomass conversion.

2. Relevant Concepts and Characteriistics of Ionic Liquids

Ionic liquid is a kind of liquid ion material at room temperature, in the common ion compounds, the Coulomb force between the ions, the size of the force and the size of the ion and the charge, the larger the radius of Yin and Yang ion, the smaller the force between them, the lower the melting point of the corresponding ion compound. Because the Yin and Yang ion radius of some ionic compounds is large, it leads to a very low melting point, at room temperature, will show a liquid state[1].

As a new catalyst, ionic liquid compared with the traditional solvent, ionic liquid has the following characteristics: First, ionic liquid mostly colorless and tasteless, vapor pressure, has good physical stability and chemical characteristics, and its liquid state temperature range is relatively broad, not volatile in 200℃ environment, so will not cause environmental pollution. Second, for most biomass has a good solubility, and also has the catalytic utility, can be used as a catalyst for many chemical reactions. Third, with strong devisability, changed by adjusting the type and proportion of Yin and Yang ions in ionic liquids, the ionic liquid can be designed to meet the needs of different systems, so it is also known as a “devizable solvent”.

3. Properties of Ionic Liquids in Biomass Conversion

In the conversion of biomass, the stability and nonvolatile properties of ionic liquids are mainly applied, so that the reaction is able to be performed under constant pressure. Ionic liquid can also dissolve cellulose, and avoid the regenerated cellulose derivative reaction, in the catalysis of fiber raw material, ionic liquid also shows a strong stability, can be recycled, so as to minimize the pollution to the environment. In addition, ionic liquid also has a very excellent performance in improving biomass reaction efficiency, because it can avoid the coordination effect of solvent and catalytic activity center Ni, so it is increasingly widely used in biomass conversion[2].

Although ionic liquids can reduce the damage to the ecological environment and are often called the “green solvent”, there are still some problems with the use of ionic liquids in the process of biomass conversion. For example, strong corrosion, relatively weak recycling capacity and high cost of use all limit the large-scale use of ionic liquids in production to some extent. Generally speaking, ionic liquid is a solvent at normal temperature. To improve its recycling efficiency, it is necessary to effectively control the separation from its products to avoid waste and loss in the process of recovery. It can make full use of its stable and nonvolatile characteristics, and develop new methods for solvent recovery.

4. Application of Ionic Liquid in Biomass Pretreatment

Pretreatment is an important link in biomass transformation, and its main function is to separate cellulose, hemicellulose and lignin which are difficult to separate from lignocellulosic biomass. In common lignocellulosic biomass, lignin is easy to form a network structure, which wraps cellulose and hemicellulose, so that cellulose can not be fully exposed during the conversion process. Therefore, the pretreatment of biomass is mainly to remove lignin on the surface of cellulose to reduce the crystallinity of cellulose and improve the use efficiency of cellulose. Among the traditional biomass pretreatment methods, physical pretreatment, chemical pretreatment and physical-chemical pretreatment are common, but they often have some shortcomings such as strong corrosivity, difficult recovery and volatile solvent, which affect the utilization efficiency of biomass conversion. Although biological method is environmentally friendly and pollution-free, it takes too long and is not conducive to industrialization. Ionic liquids, as a new green solvent, can transform and catalyze biomass with various chemical properties, and can achieve good pretreatment effect.

As early as 1934, scientists discovered that cellulose was soluble in N- ethylpyridine chloride. Since the 21st century, the high solubility of ionic liquids in cellulose has attracted wide attention in the industry, and a series of achievements have been made in the pretreatment of biomass with ionic liquids. Including single ionic liquid system and composite system, for example, the single ionic liquid system [Emim]OAc discovered by W.Y.Li[3] can have a good pretreatment effect on lignin rich in cellulose raw materials: bagasse and southern yellow pine, and can remove more than 80%

of lignin in a short time at high temperature. It can reduce lignin content and cellulose crystallization rate on wood biomass materials such as wheat straw and corn straw. S.Q.Yang[4] found that [C_2mim] ionic liquid has a strong ability to dissolve lignin in biomass, and bagasse is used as biomass, and the residual rate of lignin in 2 hours is less than 7%. However, the single system used for pretreatment often has the problem of high reaction temperature, and the ionic liquid composite system can make the reaction proceed under mild conditions. It contains "ionic liquid+water", "ionic liquid+acid" and "ionic liquid+solid acid" systems, such as: [Emim] OAc+water system, compared with single ionic liquid system, the yield of sugar reached 81% under the same conditions.J.M.Yang et al.[5] found that [Bmim]Cl-AS solvent system has a good effect on extracting cellulose from corn stalks, and the cellulose yield is as high as 74%, and the purity of regenerated cellulose is significantly improved.

5. The Specific Application

Synthetic cellulose composed of cellulose and hemi-cellulose accounts for the vast majority of the biomass, so it is important for the transformation research of cellulose under ionic liquid.This paper introduces the specific application of ionic liquid in cellulose for biomass conversion.

(1)Ionic liquid catalyzes cellulose lysis

In the direction of biomass conversion catalyzed by ionic liquids, it has always been the goal of scientists to develop catalysts with high yield of target products and mild reaction conditions. The most common catalytic system is "ionic liquid+acid" composite system, in which acids include inorganic acids, solid acids and Lewis acids.

As for the binary catalytic composite system, C.Z.Li et al.[6] developed the binary catalytic composite system with [C_4mim]Cl as solvent and inorganic acid as catalyst. It was found that the yield of reducing sugar obtained by the composite system of [Bmim]Cl and sulfuric acid was as high as 73%.

For the three-way catalytic composite system, Y.L.Zhang et al.[7] used the three-way catalytic composite system "ionic liquid+acid+water" for the first time and obtained 89% glucose yield. It is also found that the anion of ionic liquid must be Cl^- in order to have a good conversion rate of glucose. Butyl-substituted imidazole has strong catalytic ability, while allyl-substituted imidazole has better solubility but poor catalytic performance. S.Behera et al.[8] added water to the chloro-substituted imidazole system to form a ternary composite catalytic system, and found that the catalytic efficiency of hydrochloric acid was higher than that of sulfuric acid, and the yield of glucose was improved by inhibiting the formation of other products. Y.Su et al.[9] established the "bimetal+ionic liquid" catalytic system, and found that the catalytic efficiency of Lewis acid is better than that of sulfuric acid, and the catalytic efficiency of bimetal is much higher than that of metal. A.Kamimura et al.[10] constructed the catalytic system of "Li+HCl+ionic liquid". It is found that LiCl and HCl must be used at the same time to have a better catalytic effect on cellulose, as shown in Figure 1.

Whether ionic liquid plays a catalytic role or hydrolysis role in the system. A.S.Amarasekara et al.[11] catalyzed cellulose with a single ionic liquid, and found that the maximum yield was the same whether there was water or not. But after that, the team used "Lewis acid+water+ionic liquid" composite system, and the yield was improved. Therefore, ionic liquids have both hydrolysis and catalysis in this system.

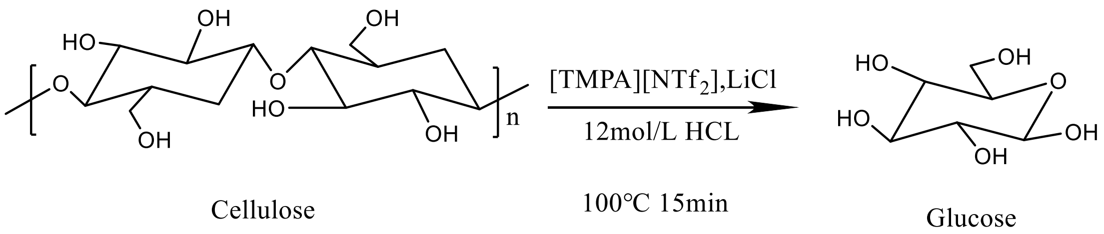

Fig.1 Li+Hcl+[Tmpa]Ntf2 the Ionic Liquid Catalytic System Catalyzes the Process of Cellulose Hydrolysis Reaction

(2) Ionic liquid catalyzes the conversion of cellulose to 5-hydroxymethyl glyphaldehyde

5- hydroxymethylfurfural (5-HMF) is a platform molecule obtained from biomass hydrolysis and widely used. It can produce a variety of high value-added chemical products and fuels through hydrogenation and esterification, such as carboxylic acid, furan, ether, alcohol, etc., so it has a very broad application prospect. Therefore, the use of ionic liquid catalytic system to catalyze the conversion of cellulose and glucose into 5- hydroxymethylfurfural has attracted wide attention from all walks of life.

The key step to convert glucose and cellulose into 5- hydroxymethyl glucuronaldehyde is to convert glucose into fructose, in which Lewis acid is commonly used to catalyze biomass into 5-HMF, and the main ionic liquid catalytic system used is Lewis acid+ionic liquid. For example, H.Zhao et al.[12] used different Lewis acids and ionic liquids to catalyze the conversion of glucose to 5-HMF, and found that chromium dichloride and [Emim]Cl were the best catalysts. The reason is that chromium trichloride ions form hydrogen bonds with glucose, which promotes the conversion of glucose to fructose. The mechanism is shown in Figure 2 below.

Subsequently, G.Yong et al.[13] added N-heterocyclic carbene NHC as ligand to study the conversion of glucose to 5- hydroxymethyl glucose furfural. The addition of nitrogen heterocyclic carbene prevents the ionic liquid from coordinating with chromium center to form crowded chromium center, which is more conducive to the combination of chromium center and glucose. The addition of nitrogen heterocyclic carbene can replace the ionic liquid, so the ionic liquid may only dissolve and catalyze the conversion of cellulose into glucose. It is also found that the Lewis acids chromium trichloride and chromium dichloride have similar catalytic effects in this system.

T.Stahlberg et al.[14] used lanthanides to catalyze glucose into HMF in ionic liquids, and ytterbium had the best catalytic effect. The effect of substituting imidazole for butyl was better than that of substituting ethyl. Subsequently, the team developed a metal-free catalyst, using “ionic liquid+boric acid” to convert glucose into 5-HMF. D.Liu et al.[15] used “Lewis acid alkyl chloride+ionic liquid” to catalyze the reaction, and found that the yield of 5-HMF was the highest in the system of triethyl chloride and [Emin]Cl. S.Suzuki et al.[16] firstly realized the conversion of fructose to 5-HMF at room temperature.

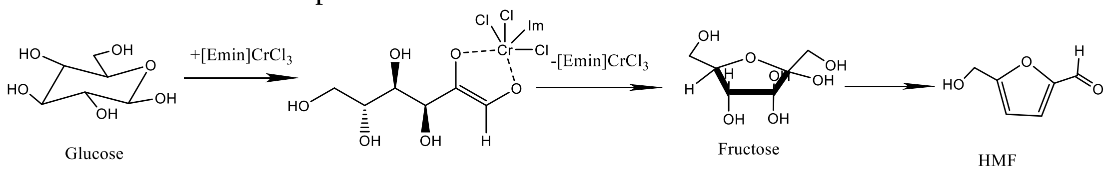

Fig.2 [Emim]Cl the Principle of Catalyzing the Conversion of Glucose to 5-Hmf

(3)Ionic liquid catalyzes the conversion of cellulose to acetylpropionic acid

Levulinic acid (LV), due to its special structure of a carboxyl group, a carbonyl group and an α-hydrogen, can be further converted into esters, alcohols, furans, ketones, etc. through hydrogenation, esterification, oxidative dehydrogenation and other reactions. Generally, to convert cellulose into levulinic acid with catalyst, the following three steps are needed (as shown in Figure 3 below): cellulose hydrolysis, glucose conversion to 5-HMF, and 5-HMF dehydration to levulinic acid.

The research shows that anions play an important role in the conversion to levulinic acid in ionic liquid catalytic system. [17,18]. Y.Shen et al.[19] studied the conversion of cellulose to levulinic acid with [BSmim] as cation, and found that the anion with the highest catalytic activity was $CF3SO3^-$.N.A.S.Ramli et al. investigated the catalytic effects of three ionic liquids on the catalytic conversion of cellulose to levulinic acid, and found that $[Smim]FeCI_4$ has the best catalytic effect because it can effectively reduce the activation energy of this reaction. Z.Sun et al. [17] catalyzed by heteropoly acid ionic liquid, and realized one-step method to catalyze levulinic acid from cellulose.

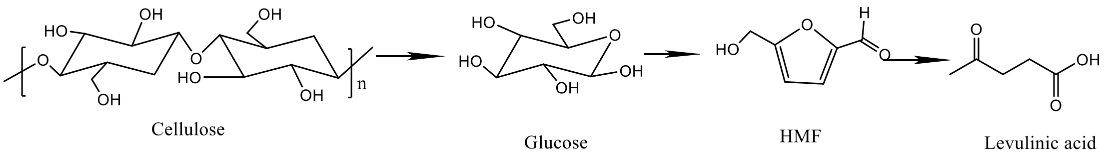

Fig.3 Catalytic Reaction Process of Conversion of Cellulose to Acetylpropionic Acid6.Conclusion

To sum up, as an important alternative to petrochemical energy, whether biomass can achieve green and clean and efficient technological breakthroughs in energy is the key to its development.The good solubility of cellulose in ionic liquid can realize the pretreatment of cellulose by ionic liquid, and better realize the biomass conversion by removing lignin. Chemical products with high added value, such as glucose, 5- methylfurfural and levulinic acid, can be formed under the catalysis of cellulose and ionic liquid composite system. At present, the most commonly used compound system is “acid+ionic liquid”. In addition, the ternary composite system of water /Lewis acid was developed to optimize the reaction conditions and increase the yield. Generally speaking, the catalytic efficiency of heterogeneous system is lower than that of homogeneous system.

Although ionic liquids have good solubility and catalytic properties, there are still some problems such as low selectivity and harsh conditions. It is of great significance to develop multifunctional ionic liquids and optimize reaction conditions.

References

[1] Chen Ru, Wang Xue, Lv Xingmei, et al.Application and Progress of Ionic Liids in Biomass Transformation [J].Light Journal, 2019,34 (3): 1-20.

[2] Waiting for Qidong, Jumeiting, Li Weizun, et al. Progress in the separation of biomass components based on ionic liquids [J].Chemical progress, 2016,35 (10): 3022-3031.

[3] LI W, SUN N, STONER B, et al. Rapid dissolution of lignocellulosic biomass in ionic liquids using temperatures above the glass transition of lignin[J]. Green chemistry (Print), 2011, 13(8): 2038-2047.

[4] Yang S, Lu X, Zhang Y, et al. Separation and characterization of cellulose I material from corn straw by low-cost polyhydric protic ionic liquids[J]. Cellulose, 2018, 25(6).

[5] Yang J, Lu X, Liu X, et al. Rapid and productive extraction of high purity cellulose material via selective depolymerization of the lignin-carbohydrate complex at mild conditions[J]. Green Chemistry, 2017, 19(9):

[6] Li C, Zhao Z K. Efficient acid-catalyzed hydrolysis of cellulose in ionic liquid[J]. Advanced Synthesis & Catalysis, 2007, 349(11-12): 1847-1850.

[7] Zhang Y, Chen X, Gu Y, et al. A physicochemical method for increasing methane production from rice straw: Extrusion combined with alkali pretreatment[J]. Applied Energy, 2015, 100(160): 39-48.

[8] Morales-delaRosa S, Campos-Martin J M, Fierro J L G. High glucose yields from the hydrolysis of cellulose dissolved in ionic liquids[J]. Chemical Engineering Journal, 2012, 181: 538-541.

[9] Su Y, Brown H M, Li G, et al. Accelerated cellulose depolymerization catalyzed by paired metal chlorides in ionic liquid solvent[J]. Applied Catalysis A: General, 2011, 391(1-2): 436-442.

[10] Kamimura A, Okagawa T, Oyama N, et al. Combination use of hydrophobic ionic liquids and LiCl as a good

reaction system for the chemical conversion of cellulose to glucose[J]. Green chemistry, 2012, 14(10): 2816-2820.
[11] Amarasekara A S, Owereh O S. Hydrolysis and decomposition of cellulose in Bronsted acidic ionic liquids under mild conditions[J]. Industrial & Engineering Chemistry Research, 2009, 48(22): 10152-10155.
[12] Zhao H, Holladay J E, Brown H, et al. Metal chlorides in ionic liquid solvents convert sugars to 5-hydroxymethylfurfural[J]. Science, 2007, 316(5831): 1597-1600.
[13] Yong G, Zhang Y, Ying J Y. Efficient catalytic system for the selective production of 5-hydroxymethylfurfural from glucose and fructose[J]. Angewandte Chemie International Edition, 2008, 47(48): 9345-9348.
[14] Ståhlberg T, Sørensen M G, Riisager A. Direct conversion of glucose to 5-(hydroxymethyl) furfural in ionic liquids with lanthanide catalysts[J]. Green Chemistry, 2010, 12(2): 321-325.
[15] Liu D D J, Chen E Y X. Ubiquitous aluminum alkyls and alkoxides as effective catalysts for glucose to HMF conversion in ionic liquids[J]. Applied Catalysis A: General, 2012, 435: 78-85.
[16] Suzuki S, Takeoka Y, Rikukawa M, et al. Brønsted acidic ionic liquids for cellulose hydrolysis in an aqueous medium: structural effects on acidity and glucose yield[J]. RSC advances, 2018, 8(26): 14623-14632.
[17] Sun Z, Cheng M, Li H, et al. One-pot depolymerization of cellulose into glucose and levulinic acid by heteropolyacid ionic liquid catalysis[J]. Rsc Advances, 2012, 2(24): 9058-9065.
[18] Dutta S, De S, Saha B, et al. Advances in conversion of hemicellulosic biomass to furfural and upgrading to biofuels[J]. Catalysis Science & Technology, 2012, 2(10): 2025-2036.
[19] Shen Y, Sun J K, Yi Y X, et al. One-pot synthesis of levulinic acid from cellulose in ionic liquids[J]. Bioresource technology, 2015, 192: 812-816.