EDITORIAL bioresources.com

Acid-Catalyzed Hydrolysis of Lignocellulosic Biomass in Ionic Liquids for Ethanol Production: Opportunities & Challenges

Shengdong Zhu,* Ke Wang, Wenjing Huang, Wangxiang Huang, Bo Cheng, Jie Chen, Rui Zhang, Qiming Chen, and Yuanxin Wu

Lignocellulosic biomass (LB) is potentially a relatively inexpensive and abundant feedstock for ethanol production. One of the most challenging steps during the lignocellulosic ethanol production is to convert the carbohydrates in LB to the fermentable reducing sugars (FRS) in an economically viable and environmentally friendly way. The acid-catalyzed hydrolysis of LB in ionic liquids (ILs) has provided a promising technical tool to improve upon the traditional FRS production process. Compared to the conventional FRS production process from LB *via* the acid or enzymatic hydrolysis method, it has many advantages, such as a simplified process, mild reaction conditions, low acid consumption, and low equipment investment. However, there are still some technical challenges that need to be solved regarding its use at an industrial scale, for example, improving its reaction selectivity, developing effective methods to separate the FRS and ILs, and alleviating the negative effect of the remaining ILs in FRS on subsequent ethanol fermentation. This editorial will give a brief discussion about opportunities and challenges of the acid catalyzed hydrolysis of LB in ILs for ethanol production.

Keywords: Acid catalyzed hydrolysis; Lignocellulosic biomass; Ionic liquid; Ethanol

Contact information: Key Laboratory for Green Chemical Process of Ministry of Education, Hubei Key Laboratory of Novel Chemical Reactor and Green Chemical Technology, School of Chemical Engineering and Pharmacy, Wuhan Institute of Technology, Wuhan 430073, PR China;
** Corresponding author: whictzhusd@sina.com; zhusd2003@21cn.com*

Acid-Catalyzed Hydrolysis of Lignocellulosic Biomass in Ionic Liquids to Improve Fermentable Reducing Sugars Production

Lignocellulosic biomass (LB) is the most abundant and renewable natural resource in the world. With ever-increasing energy demands and environmental concerns, lignocellulosic ethanol production has drawn much attention in recent years. The fermentable reducing sugars (FRS) production is one of the most important sub-processes during the lignocellulosic ethanol production. Many efforts have been made on the conversion of the carbohydrates in LB to FRS (Chen *et al*. 2014; Zhu *et al*. 2015). At present, the FRS production is mainly carried out by two different technical routes: the conventional acid hydrolysis and the enzymatic hydrolysis. The conventional acid hydrolysis is a relatively simple FRS production process, which may take the form either of a dilute acid hydrolysis process or a concentrated acid hydrolysis process. For the dilute acid hydrolysis process, it often operates at high temperature and pressure. Its main shortcomings are strong equipment corrosion, harsh operating conditions, and low FRS yields. Relatively speaking, the concentrated acid hydrolysis process can be carried out at lower temperature and has higher FRS yields. Its main problems are the strong equipment corrosion and the inadequate acid recovery. Whether the dilute acid hydrolysis process or the concentrated acid hydrolysis process is adopted, it can cause environmental problems and needs high equipment investment, which leads to the conventional acid hydrolysis unsuitable for FRS production at an industrial scale. The enzymatic hydrolysis is a relatively complicated FRS production process. Because the complex structure of lignin and hemicellulose and cellulose in LB limits its effective hydrolysis, some pretreatment procedures are needed before its enzymatic hydrolysis. Although the enzymatic hydrolysis has such advantages as high FRS yields and mild reaction conditions, the high cost of enzyme and pretreatment process limits its use at a commercial scale. To some extent, the acid-catalyzed hydrolysis of LB in ionic liquids (ILs) has the advantages of both conventional acid hydrolysis and enzymatic hydrolysis, and overcomes their shortcomings (Wang *et al.* 2011). By dissolving LB in ILs, the hydrolysis becomes a homogeneous reaction, which can be carried out under mild conditions and achieve a fast hydrolysis rate. Compared with the conventional acid hydrolysis, it has low acid consumption and low equipment investment. Moreover, it is an environmentally friendly process. Compared with the enzymatic hydrolysis, it does not need the costly enzyme and pretreatment of LB, which simplifies the process and lowers the process cost. Based on these analyses, it is clear that the acid-catalyzed hydrolysis of LB in ILs can provide a promising technical tool to improve the traditional FRS production process.

Challenges of the Acid-Catalyzed Hydrolysis of Lignocellulosic Biomass in Ionic Liquids for Ethanol Production

Since the first report on the acid-catalyzed hydrolysis of LB in ILs for FRS production (Li *et al.* 2008), there have been a number of studies aimed at improving this process for lignocellulosic ethanol production (Binder and Raines 2010; Chen *et al.* 2014). These works mainly focus on optimization of process conditions and development of novel acid catalysts (acidic IL and solid acid) to increase the reaction rate and FRS yields. Although the acid-catalyzed hydrolysis of LB in ILs presents many advantages, there are still great challenges regarding its use for lignocellulosic ethanol production at an industrial scale. The main technical obstacles that need to be solved are as follows:

(1) The reaction selectivity of the acid catalyzed hydrolysis of LB in ILs is still intermediate and needs to be further improved. The acid-catalyzed hydrolysis of LB in ILs is a complex reaction system, which involves a series of reactions. Apart from FRS, it also forms lots of byproducts, such as HMF and humus. At present, most studies to improve the reaction selectivity are based on optimization of process conditions by experience. In order to further improve the reaction selectivity, more studies should be carried out on the reaction kinetics and product control mechanism in the complex reaction system.

(2) There is still a lack of effective methods to separate the FRS and ILs in the reaction mixture at an industrial scale. Ion exchange chromatography can be used to efficiently separate the FRS and ILs at a laboratory scale, but its high cost limits its industrial use. Some reports show that solvent extraction, membrane separation, and salting out can be used to separate the FRS and ILs (Brennan *et al.* 2010). These separation methods have the potential to be used at a commercial scale, but there are still some technical problems that need to be solved to improve their separation efficiency.

(3) The remaining IL in the FRS is another problem. There are some reports that the remaining IL in the FRS has a negative effect on the subsequent ethanol fermentation process (Zhu *et al.* 2013). In order to alleviate this negative effect, more research should be performed on controlling the remaining IL concentration in the FRS, developing more IL-tolerant micro-organisms, and improving the ethanol fermentation process.

(4) There are also some problems related to decreasing the process cost of lignocellulosic ethanol production using ILs. At present, the IL is still rather expensive. More efforts should be made on lowering its synthesis cost and increasing its recycle times during the FRS production process to achieve this goal.

In conclusion, the acid-catalyzed hydrolysis of LB in ILs has provided a promising alternative to improve the lignocellulosic ethanol production, but there are still lots of technical problems that need to be solved before its industrial use. More efforts should be made on improving the reaction selectivity, developing effective methods to separate the FRS and ILs, and alleviating the negative effect of the remaining ILs in FRS on subsequent ethanol fermentation process. After our joint effort, it is reasonable to expect that an economically viable and environmentally friendly lignocellulosic ethanol production process will be established in the near future.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China No.21176196.

REFERENCES CITED

Binder, J. B., and Raines, R. T. (2010). “Fermentable sugars by chemical hydrolysis of biomass,” *Proc. Natl. Acad. Sci USA* 107(10), 4516-4521.

Brennan, T. C. R., Datta, S., Blanch, H. W., Simmons, B. A., and Holms, B. M. (2010). “Recovery of sugars from ionic liquid biomass liquor by solvent extraction,” *Bioenerg. Res*. 3, 123-133.

Chen, R., Zhu, S., Chen, C., Cheng, B., Chen, J., and Wu, Y. (2014). “Reviving the acid hydrolysis process of lignocellulosic material in biorefinery,” *BioResources* 9(2), 1824-1827.

Li, C., Wang Q., and Zhao Z. (2008). “Acid in ionic liquid: An efficient system for hydrolysis of lignocellulose,” *Green Chem.* 10(2), 177-182.

Wang, Q., Wu, Y., and Zhu, S. (2011). “Use of ionic liquids for improvement of cellulosic ethanol production,” *BioResources* 6(1), 1-2.

Zhu, S., Huang, W. X., Huang, W. J., Wang, K., Chen, Q., and Wu, Y. (2015). “Coproduction of xylose, lignosulfonate and ethanol from wheat straw,” *Bioresour. Technol.* 185, 234-239.

Zhu, S., Yu, P., Lei, M., Tong, Y., Zheng, L., Zhang, R., Ji, J., Chen, Q., and Wu, Y. (2013). “Investigation of the toxicity of the ionic liquid 1-butyl-3-methylimidazolium chloride to *Saccharomyces cerevisiae* AY93161 for lignocellulosic ethanol production,” *Polish J. Chem. Technol.* 15(2), 94-98.