# Reviving the Acid Hydrolysis Process of Lignocellulosic Material in Biorefinery

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The acid hydrolysis of lignocellulosic material (LM) is one of the most widely studied and important subprocess in the LM biorefinery. After acid hydrolysis, LM can be converted to various biofuels, biochemicals, and biomaterials through chemical or biochemical methods. However, conventional LM acid hydrolysis is not regarded as a cost-effective and environmentally-friendly process because it has drawbacks such as difficulties in acid recovery, equipment corrosion, and chemical wastes from the neutralization of acid and the removal of LM degradation products. Use of ionic liquids and solid acids during LM hydrolysis has provided potential technical tools to overcome these problems and has given new life to the LM acid hydrolysis process in the biorefinery. This editorial will discuss the role of the LM acid hydrolysis process in the LM biorefinery, provide an analysis of the conventional LM acid hydrolysis process, and briefly discuss new developments in the LM acid process.

*Keywords: Acid hydrolysis process; Lignocellulosic material; Biorefinery*

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## Role of the LM Acid Hydrolysis Process in Biorefinery

Ever increasing energy demands and environmental concerns, together with the diminishing fossil fuels reserves, have prompted increasing amounts of work toward developing convenient and efficient biorefinery platform technology to convert lignocellulosic material (LM) to biofuels, valuable chemicals, and biomaterials (Cheng and Zhu 2009). The LM is a complex mixture of cellulose, hemicellulose, and lignin that is tightly bonded by physical and chemical interactions. The LM acid hydrolysis process can effectively break down its complex structure, fractionate its components, and convert its cellulose and hemicellulose to mono-sugars (hexoses and pentoses), which can be converted to various biofuels and biochemicals via biochemical and chemical methods. The LM acid hydrolysis process can be an entry point into an LM biorefinery scheme (Rinaldi and Schuth 2009). After LM acid hydrolysis, the obtained mono-sugars as carbon source can be fermented to many products including ethanol, butanol, organic acids, and solvents (Fig. 1). They also can be chemically transformed into important biorefinery platform compounds such as xylose, furfural, 5-hydroxymethyl furfural, and levulinic acid, which can be further converted to a series of biofuels, valuable chemicals, and biomaterials. The obtained lignin can be used as cement additives, incinerated as fuel for electricity, or transformed into fine chemicals, for example, natural binders and adhesives.

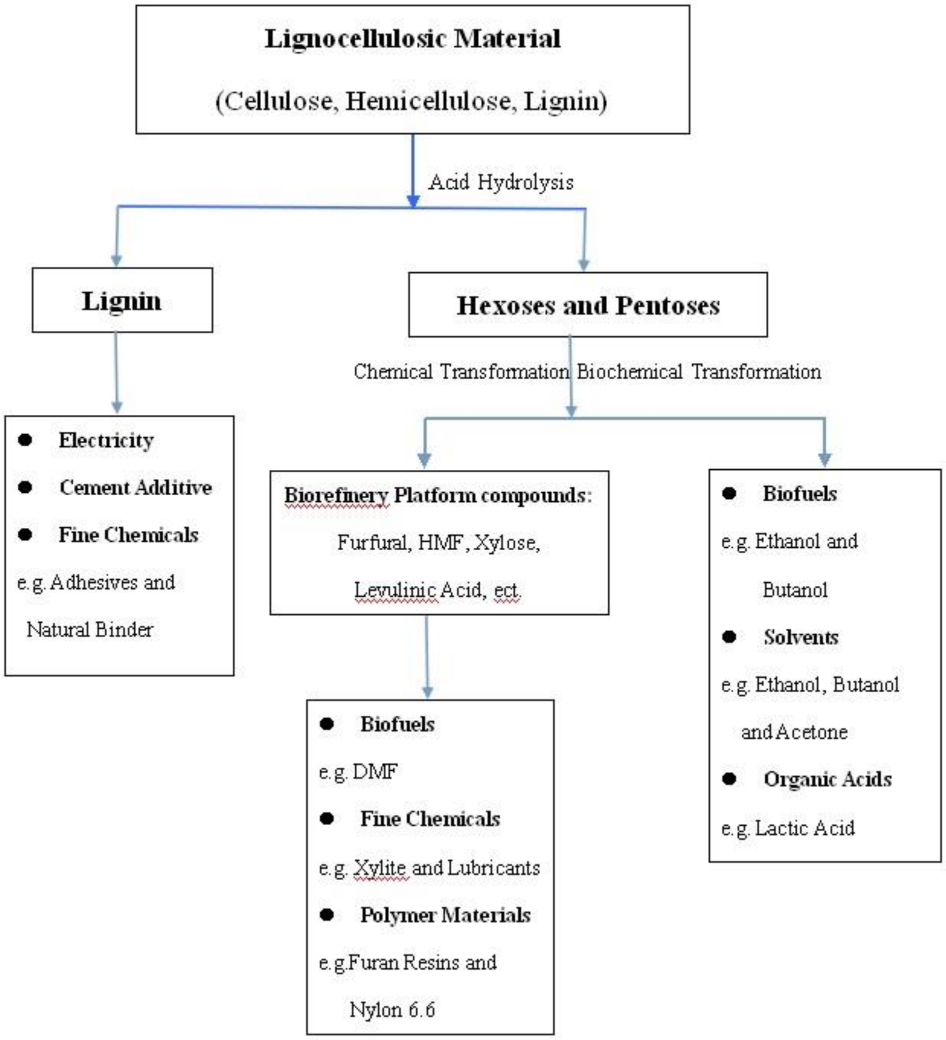


**Fig. 1.** LM biorefinery scheme based on the LM acid hydrolysis process

## Analysis of the Conventional LM Acid Hydrolysis Process

The acid hydrolysis of LM for production ethanol and chemicals has a nearly 100-year history (Taherdazeh and Karimi 2007). The conventional LM acid hydrolysis includes two kinds of processes: the dilute acid hydrolysis process and the concentrated acid hydrolysis process. The dilute acid hydrolysis process often operates at high temperature and pressure. The Scholler process is a typical dilute acid hydrolysis process. In this process, 0.5% sulfuric acid is used, and it operates at 170 $^{o}$C under 20 bar for approximately 45 minutes. The yield of mono-sugars in the hydrolyzate is only about 50% because a large amount of byproducts are formed. In order to improve this process, some efforts have been made to increase the yield of mono-sugars in the hydrolyzate and its productivity. For example, the two-stage hydrolysis system and the continuous hydrolysis operation have been developed. In spite of such progress, the dilute acid hydrolysis process still has shortcomings such as strong equipment corrosion, harsh operating conditions, and low yields of mono-sugars in the hydrolyzate. The concentrated acid hydrolysis process usually operates at room temperature with concentrated mineral acid. The Bergius process is a typical concentrated hydrolysis process. The concentrated hydrolysis process always has high yield of mono-sugars in the hydrolyzate. Its main problem is the strong equipment corrosion and the inadequate acid recovery. Although some measures have been taken to solve these problems, for example by use of gaseous HCl or anhydrous HF to facilitate acid recovery, these problems still exist. Moreover, the hydrolyzate needs to be neutralized and detoxified before it can be used to produce ethanol, whether it is from the dilute acid hydrolysis process or the concentrated acid hydrolysis process. This will increase its process cost and cause some environmental problems. Based on this analysis it is clear that the conventional LM acid hydrolysis process, whether the dilute acid hydrolysis process or the concentrated acid hydrolysis process, has its own drawbacks to become a cost-effective and environmental-friendly process in LM biorefinery.

## New Developments in the LM Acid Hydrolysis Process

To overcome the shortcomings in conventional LM hydrolysis processing, some new technologies have been adopted. Among them, the use of ionic liquids and solid acids is the most promising (Guo *et al.* 2012; Jiang *et al.* 2012; Li *et al.* 2008; Wang *et al.* 2011). Ionic liquids are a group of newly investigated organic salts that exist as liquids at relatively low temperatures (<100 $^{o}$C). Because of their non-detectable vapor pressure and high chemical and thermal stability, they are often called “green solvents”. A series of studies have shown that LM or some of its components can be dissolved in hydrophilic imidazolium-based ionic liquids such as 1-butyl-3-methylimidazolium chloride, 1-allyl-3-methylimidazolium chloride, 1-benzyl-3-methylimidazolium chloride, and 1-ethyl-3-methylimidazolium acetate (Zhu *et al.* 2006). When LM can be completely dissolved in ionic liquids, the LM acid hydrolysis process in ionic liquids is a homogeneous reaction. Compared to the conventional dilute acid hydrolysis process, the acid hydrolysis of LM in ionic liquids can be carried out under mild conditions. Compared to the conventional concentrated acid hydrolysis process, the acid hydrolysis of LM in ionic liquids needs only a trace amount of acid. This can greatly decrease the equipment corrosion and process cost. It is also a more environment-friendly process. When LM can be only partly dissolved in ionic liquids, the LM acid hydrolysis process in ionic liquids is still a heterogeneous reaction. However, some components of LM dissolved in ionic liquids changes its structure, which leads to a relatively faster LM acid hydrolysis process (Tadesse and Luque 2011). Therefore, the use of ionic liquids indeed provides new opportunities to improve the conventional LM hydrolysis process.

Besides ionic liquids, use of solid acids is another choice to improve the conventional LM acid hydrolysis process. Compared with mineral acids used in the conventional LM acid hydrolysis process, the solid acids are easily recovered from the hydrolyzate and they are also less corrosive to equipment; thus they lower the process cost and are more friendly to the environment. The commonly used solid acid in the LM hydrolysis process can be grouped into five types: H-form zeolites, transition-metal oxides, cation-exchange resins, supported solid acids, and heteropoly compounds.

Among them, the carbonaceous solid acid is considered one of the most promising because it provides good access of LM to the acidic sites of $SO_3H$ groups, which makes it have high activity and selectivity. In recent years, research studies have demonstrated that new technologies such as microwave, ultra-sonication, and nanotechnology can greatly improve the activity and selectivity during the solid acid hydrolysis of LM (Guo *et al.* 2012; Jiang *et al.* 2012). Although use of ionic liquids and solid acids present these advantages, there are still great challenges regarding their use at an industrial scale. For ionic liquid technology, more research is needed to understand the mechanism of LM acid hydrolysis in ionic liquids, and to understand how to lower their synthesis cost, to increase efficient separation ionic liquids with mono-sugars in hydrolyzate, and how to recycle the ionic liquids. For solid acid technology, more work should focus on designing solid acids having high activity, stability, and selectivity. Based on recent progress in the field, it is reasonable to expect that an efficient and economical-viable industrial LM acid hydrolysis process in biorefinery will be established in the near future.

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