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Furfural production from biomass pretreatment hydrolysate using vapor-releasing reactor system

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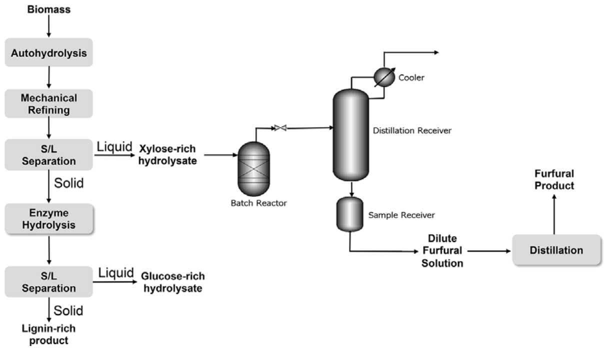
GRAPHICAL ABSTRACT



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ABSTRACT

Biomass hydrolysate from autohydrolysis pretreatment was used for furfural production considering it is in rich of xylose, xylo-oligomers, and other decomposition products from hemicellulose structure. By using the vapor-releasing reactor system, furfural was protected from degradation by separating it from the reaction media. The maximum furfural yield of 73% was achieved at 200 °C for biomass hydrolysate without the use of the catalyst. This is because the presence of organic acids such as acetic acid in hydrolysate functioned as a catalyst. According to the results in this study, biomass hydrolysate with a vapor-releasing system proves to be efficient for furfural production. The biorefinery process which allows the separation of xylose-rich autohydrolysate from other parts from biomass feedstock also improves the overall application of the biomass.

1. Introduction

One of the greatest challenges mankind is facing to in the 21st century is the depletion of fossil fuels, not only because it is our conventional source of fuel, but also because it is the primary raw material used in fine chemical engineering (Dias et al., 2005a; Lange et al., 2012). In recent years, this challenge has intrigued many researchers who have devoted themselves to the exploration and development of efficient production methodology of furanic aldehydes including furfural. It has the potential to be a sustainable substitute for petroleum-based building blocks used in the production of fine chemicals and plastics and it is usually produced via acid catalyzed dehydration of biomass-based xylose. The most important process of furfural towards upgrading to biofuel is the hydrogenation process, where furfuryl alcohol is produced. This process is usually carried out using copper-based catalysts. Hydrogenation of furfural and the formation of furfuryl alcohol may lead to many important downstream products, including levulinic acid (LA), ethyl levulinate (EL), 2-methulfuran (MF) and 2-

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methyltetrahydrofuran (2-MTHF). These downstream products have great potential of becoming fuel additive. On the other hand, the existence of formyl group in furfural structure provides a possibility for furfural to couple with other ketone or itself via condensation. Then the condensation products can undergo hydrogenation and ring opening to form long chain (C_8-C_{13}) hydrocarbons (Gandini, 2010; Lange et al., 2012). Therefore, it is necessary to establish efficient biorefinery procedures that can reduce nonrenewable fuel consumption by producing bio-based chemicals and can provide sufficient financial incentive to stimulate the expansion of the biorefining industry.

Approximately 70% of global furfural production is concentrated in China, where most manufacturers are still using the traditional methods based on homogeneous acid catalysts such as sulfuric acid and nitric acid in aqueous solutions (Karinen et al., 2011). These methods are not efficient due to the furfural resinification and are environmentally hazardous because of the solid and liquid waste generated during the production of furfural. Recently, many types of modification on the furfural production methods have been proposed. These modifications are largely focused on two aspects of furfural production: solvent system and catalyst.

Many different types of acid have been studied as catalysts in the production of furfural. Mineral acid was used in the very first furfural production process and it is still being optimized for furfural production (Agirrezabal-Telleria et al., 2014). By using hydrochloric acid as the catalyst, Chheda et al., were able to achieve approximately 65% furfural yield under 170 °C reaction temperature (Chheda et al., 2007), while Weingarten et al., estimated that based on their chemical kinetics analysis the furfural yield could reach up to 85% in a biphasic reaction system (Weingarten et al., 2011). Approximately 65% furfural yield was observed under 230 °C using sulfuric acid as the catalyst (Montané et al., 2002), while ~60% yield was achieved using phosphoric acid at 200 °C (Marzialetti et al., 2008). In order to improve the efficiency of mineral acid catalyst, inorganic salts were added to the reaction medium to enhance the furfural formation and selectivity (Marcotullio and De Jong, 2010). For example, chromium chloride ($CrCl_3$), which is a Lewis acid, has been used with hydrochloric acid, a Brønsted acid, to accelerate furfural production resulting in an overall furfural yield of 39% (Yang et al., 2012).

Another important type of acid catalyst that has been widely adopted in furfural production is solid acid. H-ZSM zeolite, for example, was tested in its protonated form for catalyzing furfural production. It was observed that under 200 °C, in a pure aqueous environment, a yield of 46% could be achieved (O'Neill et al., 2009). It was also reported that H^+-mordenite can catalyze the conversion of pentose into furfural at high temperature (260 °C) and 55 atm with a molar furfural yield of 98% and a furfural selectivity of 98% (Lessard et al., 2010). For zeolite solid acid catalysts, the ratio between the number of Lewis acid sites and Brønsted acid sites significantly affects the conversion of sugar and the yield of furfural (Weingarten et al., 2011). In addition to zeolite, whose pore size is approximately 5–13 Å, mesoporous materials such as MCM-41 and SBA-15 which have larger pore sizes around 2–50 nm have also been studied as catalyst for furfural production. It has been shown that MCM-41 in its HSO_3^- functionalized form can catalyze furfural production in a water/toluene biphasic system to obtain a furfural yield of ~76% at 140 °C (Dias et al., 2005b). Recent reports have suggested that SBA-15-HSO_3 can also be used to obtain a furfural yield of ~70% at 160 °C (Shi et al., 2011). Ion exchange resin, which is another type of solid acid, has also been studied as a catalyst in reactions aiming to convert xylose to furfural. For example, a furfural yield of 70% was observed while using Amberlyst 70 as a catalyst in water/toluene system (Agirrezabal-Telleria et al., 2011).

In addition to designing novel acid catalysts, recent studies have also emphasized on exploring the solvent system for furfural production. Currently four types of solvent system are being employed the most in this field: water, organic solvents, water-organic bi-phase system and ionic liquid (IL). Gürbüz et al., starting from xylose, recently used H^+-mordenite as the solid acid catalyst and obtained 100% sugar conversion with 81% furfural yield in gamma-Valerolactone (GVL) solvent (Gürbüz et al., 2013). With water as the sole solvent, Antunes et al., using H-MCM-22 zeolite and ITQ-2 solid acid, achieved 71% furfural yield with 96% sugar conversion at 170 °C (Antunes et al., 2012). Aqueous-organic bi-phase solvent systems were introduced into furfural production because it is believed that the organic phase can take the generated furfural away from the reaction center (catalyst surface), so that the side reaction in which furfural interacts with xylose to form humins could be suppressed. Many organic solvents have been tested in tandem with water in furfural production. Some combinations have included mixtures of the following solid acids with water: MIBK (Dias et al., 2005b; Weingarten et al., 2011), toluene (Agirrezabal-Telleria et al., 2011; Antunes et al., 2012; Shi et al., 2011), and 1-butanol (Zhang et al., 2012). Ionic liquid is another solvent system that has also been introduced into furfural production. It has been shown that in an ionic liquid system, the generated furfural is more stable which leads to a higher yield (Matsagar et al., 2015; Serrano-Ruiz et al., 2012; Sievers et al., 2009).

Through these modified methods, higher sugar conversion and furfural yield were achieved. However, there are a number of drawbacks associated with these methods such as the high price of ionic liquid and bi-phase solvent systems, solid acid deactivation due to humins deposition, and active site loss. This is why these methods have not been widely put into practice in the furfural industry yet. While working towards the goal of designing efficient, environmental friendly, and financially incentivizing biorefining procedures, we designed a biorefinery scheme where the aqueous solution produced by biomass autohydrolysis is used as the input feedstock. By employing a simple aqueous solvent environment without an acid catalyst, relatively high sugar conversion as well as furfural selectivity was achieved. Compared to traditional furfural production procedures, an additional step in which furfural and steam released from the reactor are added to improve the selectivity of furfural and suppress the side reaction between xylose and generated furfural by using the vapor-releasing Parr reactor system. The vapor releasing procedure was carried out by connecting a Parr reactor with a condenser to collect the furfural vapor product.

Lignocellulosic biomass is the primary feedstock used for furfural production in industry today. Depending on the type of biomass, the pentosan content ranges between 6% and 32% of the total amount (Zeitsch, 2000). Corncob has been wildly used in China for furfural production because of its rich hemicellulose content and relatively cheap cost. However, the serious environmental pollutants created by the use of mineral acid along with the gradual increase in the price of biomass have made the process less attractive than before. Even though feedstock like corncob is rich in pentosan, there is still a large portion of lignocellulosic biomass left as residue after furfural production. Huge amounts of biomass waste are produced in all traditional furfural production process because they cannot fully consume the cellulose and lignin content in feedstock. To solve this problem, one may refine the biomass feedstock and only use the liquid after pretreatment for furfural production. A biomass refinery process including autohydrolysis pretreatment, machine refining, and enzymatic hydrolysis allows for the efficient separation of hemicellulose, cellulose, and lignin content from the raw biomass(Han et al., 2015; Huang et al., 2016; Jones et al., 2013). The liquid obtained after autohydrolysis is the so-called "hydrolysate" in which dissolved hemicellulose is the dominant component. The solid obtained after pretreatment contains mainly cellulose and lignin, which are both great sources for the production of high-valued chemicals such as 5-HMF, levulinic acid from cellulose and aromatic compounds from lignin (Cai et al., 2014).