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Liquid phase reforming of rice straw for furfural production

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ABSTRACT

In this study, rice straw was employed in liquid-phase reforming for furfural production. Rice straw was hydrolyzed with acid, ethanol, methyl-isopropyl ketone (MIPK), and water in an autoclave, and then reacted at 140 °C. Cellulose, hemicellulose, and lignin were extracted, and their contents were determined. The Taguchi method was employed to obtain the optimal operation conditions for xylose dehydration. The optimal operation conditions were modified again to reduce costs and then applied to rice straw hydrolysate dehydration.

The maximum furfural yield of the sample reaction using xylose solution was 35.19% at 200 °C reaction temperature and 3 wt% hydrochloric acid added. The optimal operation conditions were 60 g/L initial xylose concentration, 150 °C reaction temperature, 0.75 g of Pt/Al₂O₃, and 5 wt% hydrochloric acid. Rice straw hydrolysate dehydration showed similar results with xylose dehydration. All additives (ethanol, MIPK and Pt/Al₂O₃) could be recovered and reused. Therefore, the method has promising future industrial applications. Copyright © 2013, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Rice straw, one of the most abundant agricultural wastes in the world, has a promising viability as an economical and environment-friendly energy resource [1]. The annual production of rice straw around the world is estimated to be 600–900 million tons per year [2]. At present, the major disposal method for rice straw is field burning, which inevitably aggravates air pollution problems. Consequently, this issue has gained global attention. Rice straw is a lignocellulosic material generally consisting of cellulose (32%–47%), hemicellulose (19%–27%), lignin (5%–24%), and inorganic components (5%–10%) [3,4]. Cellulose, hemicellulose, and lignin all have high availability in the future. However, their

extraction from raw materials is challenging. Generally, lignocellulose can be hydrolyzed by the concentrated acid, diluted acid, steam explosion, and enzymatic methods. Our previous study [5] has revealed that pentoses (including xylose and arabinose) can be easily obtained by the dilute-acid hydrolysis method. Huber et al. [6] have pointed out that hydrolysis degradation is favorable for separating cellulose, hemicellulose, and lignin from cellulosic biomass (i.e., wood, wood wastes, corn stover, switch grass, agricultural wastes, and straw). Dilute-acid hydrolysis is generally desirable because of its low cost. It also allows the high degradation of lignocellulosic biomass under relatively low reaction temperatures. A typical lignocellulose hydrolysis process usually consists of two stages [2], i.e., the hydrolysis of hemicellulose

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from raw materials and the hydrolysis of cellulose from the residues of the first step. Theoretically, 41.0%–43.4% glucose, 14.8%–20.2% xylose, 2.7%–4.5% arabinose, 1.8% mannose, and 0.4% galactose can be obtained in the rice straw hydrolysate [5].

In the first stage, the dilute-acid hydrolysis of lignocellulose is normally operated at 100–200 °C with auto-generated pressure for several seconds to minutes. Furfural and 5-hydroxymethyl furfural are also generated during the process due to the further dehydration of xylose and glucose. Furfural is widely used as an important chemical raw material for pesticides, pharmaceuticals, food additives, and so on. It can also be used as a raw material for refined petroleum, oil, and solvents for various industrial applications [7]. Furfural production is already established in various industries for the past 80 years; however, a synthetic route has not yet been discovered. Weingarten et al. [8] have investigated an intrinsic kinetic model for the dehydration of xylose. They have suggested four possible reactions: (1) dehydration of xylose, (2) furfural and xylose reaction to form solid humins, (3) furfural self-reaction to form solid humins, and (4) extraction of furfural into organic solvent. The activation energy of the dehydration reaction ($E_A = 124 \text{ kJ mol}^{-1}$) is much higher than that of the humins formation from reaction 2 ($E_A = 72 \text{ kJ mol}^{-1}$) and reaction 3 ($E_A = 68 \text{ kJ mol}^{-1}$). Consequently, side product formation is inevitably avoided in the xylose dehydration reaction.

Furfural is generally produced from pentose, which can be extracted from lignocellulosic agricultural waste [9,10]. Approximately 10% of the raw material can be converted into furfural. Furfural production is widely studied in laboratories [3,10–19]. The addition of heterogeneous catalyst to the reaction for furfural production is well known to reduce the activation energy as well as the reaction temperature, and enhance the reaction rate. Thus, heterogeneous catalysts improve the overall performance for furfural production. Numerous heterogeneous catalysts (i.e., Fe_2O_3 , ZrO_2 , ZnO , TiO_2 , Al-MCM-41, zeolite, and amberlyst) and their effects on furfural production have been discussed [19–22].

The present study employed rice straw as the raw material for furfural production. As aforementioned, the reaction involves many side reactions. To reduce such technical problems, xylose is used as feedstock in preliminary studies. A Taguchi L9 orthogonal array was also employed due to its simple design and convenient discussion. Based on the results of the preliminary studies, the rice straw hydrolysate was used in furfural production and its viability was studied. The effects of some parameters on the dehydration reaction for furfural production and in the hydrolysis reaction for xylose production were investigated.

2. Experimental

2.1. Hydrolysis and dehydration

The schematic diagrams of the rice straw hydrolysis and dehydration processes are shown in Fig. 1. Both reactions were carried out in an autoclave reactor (ss-316, ca. 500 ml).

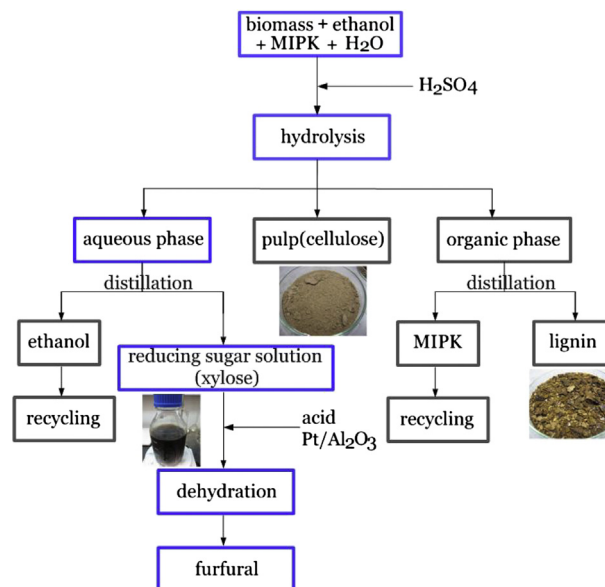


Fig. 1 – The schematic processes of the liquid phase reforming in this study.

Ethanol and methyl isopropyl ketone (MIPK) were used in the hydrolysis process to separate cellulose (residual), hemicellulose (reducing sugar solution, aqueous phase), and lignin (organic phase) from the raw hydrolysate [23,24]. The rice straw was naturally dried for several days, ground, dried at 65 °C, and stored in a sealed container prior usage. Prior to hydrolysis, 40 g of rice straw (particle size < 0.35 mm) was soaked in a solution containing 45 ml of H_2SO_4 (6 M), 176 ml of MIPK, 128 ml of ethanol, and 56 ml of distilled water, respectively. The mixture was then heated to 140 °C at a 2 °C/min heating rate and maintained at this temperature for 56 min. The mixture was cooled by water to room temperature. The reducing sugar solution and lignin were extracted by the distillation of the liquid- and organic-phase solutions, respectively, where ethanol and MIPK were also recovered. After the rice straw hydrolysis process, the hydrolysate (reducing sugar solution, approximately 70% xylose) was then applied to the dehydration reaction for furfural production.

As aforementioned, the dehydration of xylose for furfural formation is complicated. To simplify the preliminary studies, xylose (Acros) solution was employed. A Taguchi L9 orthogonal array was also employed to investigate the effects of xylose concentration, $\text{Pt/Al}_2\text{O}_3$ (1 wt%, 1/8" pellet, Alfa Aesar), reaction temperature, and acid amount. Prior to the dehydration reaction, a total volume of ca. 200 ml of solution (containing xylose, distilled water, and acid) was poured into an autoclave reactor. The solution was heated to the setting temperature at a heating rate of 2 °C/min. After the reaction temperature reached the setting temperature, the products were sampled every 15 min for 2 h. Based on the preliminary studies, the optimal reaction conditions were obtained and applied to the dehydration of rice straw hydrolysate for furfural production.

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