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Effects of solvents and catalysts to furfural production from xylose dehydration reaction

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Abstract: Furfural is industrially produced from lignocellulosic biomass via hydrolysis/dehydration reactions or C_5 sugars (pentoses) via dehydration reaction in aqueous acidic media. Nevertheless, the corrosion problem and side reactions are major problems of this production process. The aim of this work was to study the effects of solvents and catalysts to furfural production from xylose dehydration reaction under biphasic batch reaction system. The study compared two solid acid catalysts (zeolite beta and ZSM-5) and three high boiling point solvents (ethylene glycol, dimethyl sulfoxide and sulfolane). The experimental results revealed that sulfolane and ZSM-5 showed a good performance for furfural production because they provided the highest furfural yield (49.1%) and prevented the occurrence of side reactions. The highest furfural yield (54.8%) from xylose dehydration was achieved at 200 °C with the reaction time of 90 min over ZSM-5 catalyst in sulfolane. For catalyst recycling studies, ZSM-5 catalyst could also be reused up to 4 cycles with a yield of 51%.

Keywords: Xylose dehydration, furfural production, zeolite beta, ZSM-5, sulfolane.

1. Introduction

Furfural (C_4H_3O-CHO) or 2-furaldehyde is a chemical substance that can be produced from sugarcane bagasse. It is an organic compound, colorless liquid, water-soluble and has a boiling point of 161.8 °C. It is an important chemical intermediate in many industries to produce other high value products. Typically, furfural is used in resin production and lubricant production. Furthermore, furfural can be an initial substance to produce furfuryl alcohol that is important in pharmaceutical, agricultural and petroleum industries. Recently, the people are interested in furfural production because it can be produced from biomass residue consisting of hemicellulose such as corncobs, rice straw, wheat bran and sugarcane bagasse. In other words, instead of throwing away biomass residue, people can increase the value of biomass with renewable feedstocks.

The methods of furfural production have two reactions: hydrolysis reaction of sugarcane bagasse to hemicellulose by acid solution and dehydration reaction by an acid catalyst. The main component of hemicellulose is polysaccharides. Therefore, it is easy for hemicellulose to transform its structure into 5-carbon sugars (xylose) used to produce furfural. Nowadays, many industrial of commercial furfural productions develop by Quaker Oats technology [1]. The process is a batch or continuous model and it use sulfuric acid as a mineral acid catalyst at low temperature conditions. The advantages of this process are low energy consumption which results in low production costs. Yazdizadeh et al. investigated the method uses batch reactor to produce furfural. The main raw material is pentosan-rich plant from bagasse. Using sulfuric acid as a catalyst with inorganic salt ($NaHSO_4$) for promoter. The reactor is heating up to 160 °C for 7 minutes. The process obtains 5-10% of furfural yield from the top as a vapor [2]. However, it has a lot of problems such as equipment corrosion from catalyst acid, difficulty to separate a catalyst from product and poor yield of furfural because of equilibrium limitation. So, the method of traditional furfural production has to find the solution for this problem and can be applied on a commercial scale.

Mittal and Sato applied a biphasic system by using a biphasic batch reactor to produce furfural. Biphasic solvent system containing the aqueous reactive phase and the organic phase. The main raw material is xylose and solvent such as MIBK, toluene and cyclohexanol. Two experiments, using different catalysts that are sulfuric acid and ion-exchange resin (Amberlyst 70). The maximum furfural yield from each experiment is 77% and 40.9% [3-4]. This method represents the advantage of the biphasic system can enhance furfural production and removes furfural from the reaction zone. O'Brien studied continuous furfural production by using high-temperature conditions around 220°C with continuously feeding raw material. The advantage contains short residence time, high concentration of furfural in the vapor products and acid catalyst can be recovery. The furfural yield obtained around 50-70% [5]. On the other hand, this method is high cost of investment and maintenance.

The reaction temperature is one of the important factors to produce furfural because it involves energy to use in reactor equipment. In the case of high reaction temperatures, a lot of energy is consumed in a process that results in a loss of energy cost. Consequently, Raman and Gnansounou studied effect of the reaction temperature in furfural production. They reported changing xylose into furfural, the conversion increase with a high temperature. At extreme temperature, the xylose and furfural are significantly converted to humin. The temperature exceeding 170 °C, fufural yield decrease to the thermal instability of furfural at extreme temperatures [6]. In addition, Wang et al. indicated that reaction temperature is an important factor to influence dehydration reaction. In this study, using difference temperature from 130-210 °C for 60 min under microwave irradiation in a batch process to investigate the optimum temperature with sulfonated sporopollenin (SSP) as a catalyst. At a temperature below 180 °C, the conversion and furfural yield are poor. Interestingly, the maximum furfural yield is 56% at 190 °C which completes the conversion of xylose [7]. Moreover, at a temperature higher than 170 °C, humin formation is observed in the system that causing to low furfural yield similar to the result of Raman and Gnansounou.

The reaction time is the one-factor impact on furfural production in industries scale. Wang et al. presented the reaction time has a crucial effect on furfural yield. In this study, the reaction time from 10-80 minutes is investigated at 180-190 °C. The conversion of xylose increase with the reaction time which maximum of furfural yield is 56% (190 °C) at 40 minutes and 53% (180 °C) at 70 minutes [7]. From the result at high temperature is significant to reduce reaction time for dehydration of xylose with sulfonated sporopollenin (SSP) as a catalyst in a batch process. In the same way, the factor of the reaction time is involved reaction temperature which should balance two value to obtain the optimum condition in the process.

From the research, the many conditions had an effect on furfural production whether solvent, catalyst temperature, time, etc. Thus, this work focuses on finding the optimum condition including solvent, catalyst, reaction temperature, and reaction time to increase furfural yield production. However, this research integrated two advantage methods that are biphasic systems with solid acid catalysts to improve furfural production. It is expected that the optimization process under biphasic batch reaction system would begin switch from batch to continuous process and then scale up the process to industrial scale.

2. Materials and Method

2.1 Chemicals

Xylose and furfural were analytical reagent grade and purchased from Ligand Scientific Co., Ltd., respectively. Ethylene glycol (EG), dimethyl sulfoxide (DMSO), and sulfolane were obtained from Ligand Scientific Co., Ltd., respectively.

The zeolite catalysts, zeolite beta (Si/Al molar ratio = 25, surface area = 680 m^2/g) and ZSM-5 (Si/Al molar ratio = 250, surface area = 400 m^2/g) were purchased from Ligand Scientific Co., Ltd., respectively.

2.2 Product analysis

In this experiment, the concentrations of xylose and furfural were analyzed by high performance liquid chromatography (HPLC) on a Biorad Aminex (HPX-87H) column using a refractive index detector (RID) (column heated to 65 °C, 5 mM H_2SO_4 as a mobile phase at 0.5 mL min^{-1}). After that, the results were calculated in terms of conversion and yield based on equations (1) and (2) below.

$$\%\ \text{Xylose conversion} = \frac{\text{weight of xylose feedstock (g)} - \text{weight of xylose in product (g)}}{\text{weight of xylose feedstock (g)}} \times 100 \quad (1)$$

$$\%\ \text{Furfural yield} = \frac{\text{weight of furfural in product (g)}}{\text{weight of xylose feedstock (g)}} \times 100 \quad (2)$$

2.3 Reaction testing

The reactions were carried out in a batch-type reactor (Parr's Reactor) with inner volume of 150 cm^3. A typical procedure was as follows: xylose feedstock (2.5 %wt. of xylose solution or 3.75 g) and solid catalyst (0.1875 g), and biphasic solvent systems (water/organic solvent = 40:60 %v/v, 135 mL) were introduced into the reactor. N_2 was loaded to raise the reactor pressure to 1 MPa. Then, the reactor was heated at 200 °C and the reaction time (60 min) was counted after the inside temperature of reactor reached 200 °C.

After that, the best catalyst and solvent were selected for finding the optimum condition that including reaction temperature and reaction time. The reaction temperature was varied in the range of 160-220 °C. The reaction time was varied in the range of 30-120 minutes.

3. Results and Discussion

3.1 Effect of solvent systems

A reaction was done in the biphasic system by using water: high boiling point organic solvent ratio of 40:60 %v/v (135 mL) on furfural production at 200 °C for 60 min in non-catalytic reaction. From experimental results, the xylose conversion of total solvent systems on non-catalytic was in the range of 70% to 80%. It shows that the dehydration reaction of xylose was easily occurring at high temperatures. All of the solvents showed effects on furfural yield. The maximum values were about 30% derived from sulfolane and DMSO as a result of water-immiscible solvents, preventing furfural mix in the water phase [3]. In addition, sulfolane could be prevented the condensation of humin in the equipment by dissolving humin [8]. Humin is carbonaceous, polymeric by-products formed during acid-catalyzed dehydration of sugars [9]. Therefore, sulfolane was selected as the optimum solvent for applying with subsequent steps.

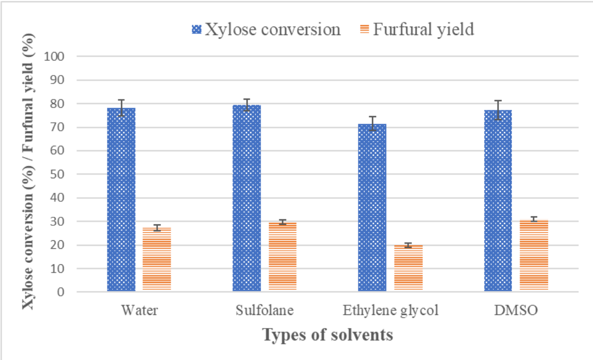

Figure 1. Effect of solvent systems on non-catalytic dehydration of xylose in water/sulfolane, Ethylene glycol, DMSO biphasic system at 200 °C.

3.2 Effect of catalyst types

In the experiment, the 2.5%wt solid acid catalysts of xylose were used to increase furfural yield in the water/sulfolane biphasic system. The results of various solid acid catalysts including zeolite beta and ZSM-5 are shown in figure 2 in terms of xylose conversion and furfural yield.

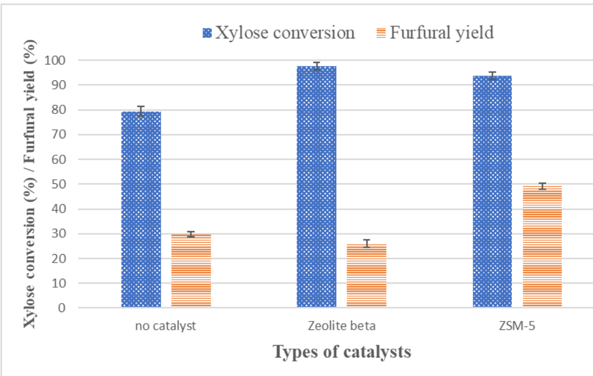

Figure 2. Effect of catalyst types from dehydration of xylose in water/sulfolane biphasic system at 200 °C for 60 min.

From the results, a conversion increases 10% to 20% when compared with a non-catalytic reaction in a batch process. Two types of catalysts were commercial catalysts but different a ratio of silicon dioxide (SiO_2) and aluminum oxide (Al_2O_3). The ZSM-5 has higher Si/Al ratio than zeolite beta, resulting in weaker acidity. The maximum furfural yield achieved in ZSM-5 is around 49.1% because of its appropriate acidity [10]. For this reason, ZSM-5 was selected as the optimum catalyst for promoting dehydration reaction of xylose and applying with advanced technique. However, it had to investigate the number of cycles for catalyst deactivation in subsequent steps to reduce catalyst cost in the furfural production.

3.3 Effect of reaction temperature

The experiment found that the reaction temperature was a significant factor to enhance furfural yield in the process. In this study, variation of temperature from 160 °C to 220 °C for 60 minutes was investigated in order to determine optimum reaction temperature by ZSM-5 in water/sulfolane biphasic system.

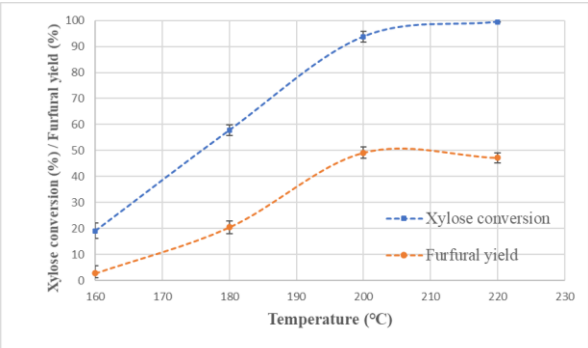

Figure 3. Effect of reaction temperature from dehydration of xylose catalyzed by ZSM-5 in water/sulfolane biphasic system at 160-220 °C for 60 min.

As shown in figure 3, The results indicate that an increase in the reaction temperature cause a significant increase in the xylose conversion. In addition, xylose conversion obtained 210 °C and 220 °C were quite not different. It indicates that the dehydration reaction of xylose was quite a complete reaction at high temperatures. However, the dehydration reaction at high temperature had still a problem with humin formation. For this reason, humin influences a decrease in furfural yield. Moreover, the humin formation affected catalyst deactivation on the catalyst surface. It causes that the xylose molecule could not enter to react on the surface of the catalyst. Hence, the optimum reaction temperature was 200 °C that provided the maximum value of 49% furfural yield.

3.4 Effect of reaction time

In a previous literature study, the reaction time was an important factor effect on furfural production in a batch process [7]. In this experiment, the reaction time was investigated in a range of 30 minutes to 120 minutes by ZSM-5 in water/sulfolane biphasic system at 200 °C. The results are shown in figure 4 in terms of xylose conversion and furfural yield.

As present in figure 4, it was observed that the xylose conversion considerably increased from 60% to 95% at 30 minutes to 60 minutes of reaction time. After that, the dehydration reaction of xylose had completely, resulting in 100% of xylose conversion at 120 minutes reaction time. On the other hand, when increasing the reaction time more than 90 minutes, the furfural yield was declined due to occurring furfural react with xylose or itself through resinification and condensation reactions [11]. Hence, the optimum reaction time of 90 minutes provided the maximum value of 54.8% furfural yield.

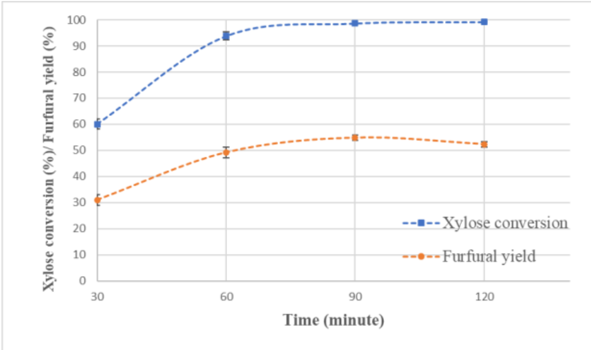

Figure 4. Effect of reaction time from dehydration of xylose catalyzed by ZSM-5 in water/sulfolane biphasic system at 200 °C.

3.5 Catalyst reusability

The catalyst was an important factor for investment cost in furfural production. Consequently, this experiment also investigated the catalyst reusability. The optimum condition was sulfolane as a solvent, ZSM-5 as a catalyst, reaction temperature at 200 °C and reaction time 90 minutes. The results are shown in figure 5 in terms of xylose conversion and furfural yield.

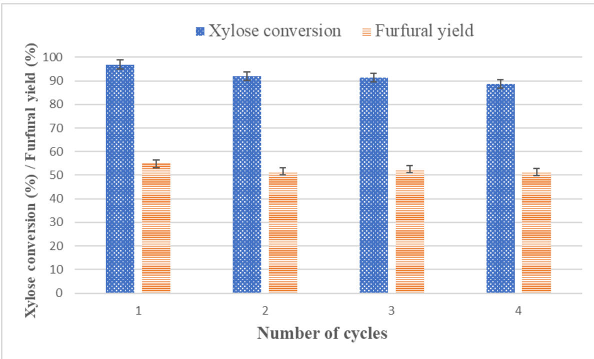

Figure 5. Effect of reusability from dehydration of xylose in 4 consecutive runs catalyzed by ZSM-5 in water/sulfolane biphasic system at 200 °C for 90 min.

The results shown that the catalyst was reused 4 times which can be found in the second cycle when compared with the first cycle. The furfural yield decreased around 10% due to humin formation resulting to block on the surface of the catalyst [8]. After that, in the next cycle for reused catalyst 4 times, it can be observed that xylose conversion and furfural yield slightly reduced. Therefore, ZSM-5 catalyst could be reused up to 4 cycles with a yield of 51% in the furfural production process. However, the catalyst regeneration process should be investigated for appropriate catalyst reusability in furfural production.

4. Conclusions

The effects of solvents and catalysts to furfural production from xylose dehydration were experimentally studied. The results showed that the conversion of xylose can convert easily. However, to achieve furfural with high yield, the selectivity must be improved. The experimental results revealed that sulfolane and ZSM-5 can improve the desired product yield because they can prevent the occurrence of side reactions. The best reaction condition for furfural production was observed at 200 °C with the reaction time of 90 min over ZSM-5 catalyst in sulfolane, providing furfural yield of 54.8%.

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