Production of Furfural from Oil Palm Frond via Green Chemicals Using Supercritical Ethanol and Formic Acid

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This research aimed to study the potential of furfural production via green chemicals (supercritical ethanol and formic acid) using oil palm biomass. Furfural was obtained via reaction conducted using a high-pressure and high-temperature mini-batch reactor. Various reaction parameters were studied including temperature, reaction time, solid loading, and alcohol-acid ratio. Depolymerisation of the pentosan into xylose by supercritical ethanol and subsequent dehydration of xylose into furfural from the acid-catalyzed reaction occurred simultaneously in the mini-batch reactor. Results obtained showed the highest furfural yield of 88.7% at 260°C, 10 min, 0.6 g solid loading, and 1:2 alcohol:acid ratio. The highlight of this research is in the use of green chemicals in which a fully biomass-based process were achieved as both ethanol and formic acid can be produced from biomass itself. Ethanol is produced by fermentation of saccharides. Meanwhile formic acid is generated from furfural production itself.

Key Words
Furfural, biomass, Oil palm frond, Supercritical liquid, Acid-catalyzed reaction

1. Introduction

Furfural is biomass-derived chemical that is used to replace petrochemicals. It can be used as biofuels to reduce the carbon dioxide emissions and to replace fossil fuel as its resource. In addition, furfural acts as various value-added chemical additives. Furfural is derived from lignocellulosic biomass. In furfural production, the linking between hemicellulose is broken down to release the sugar component (xylose). However, before the xylose monomers are released, its main fragment also known as pentosans (five carbon polysaccharides) contained in the hemicelluloses is hydrolysed through acid-hydrolysis reaction. Furfural is subsequently formed by removing three water molecules through the dehydration process. The characteristic of pentosan, which has higher solubility in acid compared to crystalline cellulose allowed it to hydrolyzed and dehydrated to furfural faster than glucan from cellulose. Due to this, lignin and glucan will settle down as the solid residue at the end of the reaction.

The current complication in furfural production is the availability of raw material. Current research on furfural production used biomass such as corn cobs, sugar cane bagasse, rice straw, timber varieties, and Switchgrass. In commercialized production of furfural, China, Dominican Republic, and USA are the largest producers of furfural presently. The raw materials resources are corn cobs and oats biomass. The main idea of this research is to utilize oil palm biomass as the source of raw materials in the production of furfural. Currently, Malaysia is the second largest in palm oil production, hence the large amount of biomass produced from these oil palm plantation. The breakdown of wastes from oil palm plantation and production in year 2007 is shown below in Table 1. This abundant supply can be converted into value-added product such as furfural. Furfural has tremendous potential as it can act as a chemical platform for production of various types of bio-fuels and bio-chemicals.

This study focused on using green chemicals (ethanol and formic acid) to produce furfural. Furfural is produced in industry by using mineral acids (sulfuric acid and phosphoric acid) with lignocellulosic feedstocks under hydrothermal conditions. However, this method has severe limitations resulting in significant loss of furfural yield during production, as well as other setbacks such as corrosion.
of pipelines and valves at high temperatures, safety issues, cost and environmental issues due to hazardous waste effluents as a result of using mineral acids in the reactions. Antal et al. (1991) reported furfural yield in the range of 21-63 mol% using sulfuric acid-catalysed dehydration of pure xylose in subcritical water. Aguilar et al. (2002) studied sulfuric acid hydrolysis of sugar cane bagasse at 100-128 °C with 2-6% acid concentration. They observed a direct correlation between furfural yield with temperature. The increase in temperature enhanced the formation of furfural. They further suggested this is due to the increase in the decomposition of xylose from the biomass.

Previous studies established that furfural could be produced through acid-catalysed reaction mainly from minerals acid. In this study, formic acid is used to replace minerals acid, commonly used in furfural production. The use of formic acid for acid-catalysed hydrolysis and its subsequent dehydration of xylose from hemicellulose to produce furfural have been proven as an effective process. In addition, formic acid is found to be one of the by-products during the furfural process itself through the cleavage of formyl group or the hydrolytic fission of the aldehyde group of furfural. Therefore, the process is essentially self-sustainable since the formic acid produced during the reaction can be recycled back into the process as catalyst. The utilization of organic acid will eliminate the drawbacks of mineral acid catalysts such as industrial pollutant emissions.

Supercritical liquids exhibit a wide range of chemical and physical properties, varying from gas-like to liquid-like behaviour. This ability to obtain different properties by manipulations of its temperature and density owing to significant variations in the ionic product and dielectric constant has led to increased attention on its use especially supercritical water as a medium for reaction especially in the gasification and liquefaction of biomass to produce renewable fuels as well as chemicals. However, the high critical temperature and pressure of water is a major concern in the production industry. On the other hand, the critical temperature and pressure of alcohols such as ethanol is considerably lower (>243 °C and 6.38 MPa) and therefore offers milder conditions for the reaction. In addition, at ambient conditions, ethanol has a dielectric constant of 24.5. This allows moderate solubility for many kinds of polar and ionic substances. However, the dielectric constant decreases substantially with increasing temperature. The significant decrease of the dielectric constant at the critical point can dissolve many kinds of non-polar organic substances. Therefore, the use of supercritical ethanol as solvent is expected to readily dissolves and breaks the linkages between lignin and hemicellulose thus rendering it assessable for acid-catalysed hydrolysis. In addition ethanol is a green solvent since it can be produced from biomass itself through fermentation of saccharides. Therefore, the proposed reaction is 100% biomass-based without the addition of any synthetic chemicals.

Hence, the main aim of this study is to study the feasibility of producing furfural from oil palm fronds using supercritical ethanol and formic acid. The effects of 4 reaction parameters (biomass solid loading, alcohol-acid ratio, reaction temperature and reaction time) towards the furfural yield were investigated.

2. Experimental

The oil palm fronds were obtained from a plantation at Felda Pasoh Tiga, Negeri Sembilan, Malaysia. The raw materials were placed into a drying oven at 45 °C for 3 d and cooled down to room temperature. The oven-dried fibers were then grounded using heavy-duty blender until the entire samples passes through the 1.0 mm sieve screens. This is to ensure the uniform particles sizes. The chemical composition of the oil palm fronds is shown in Table 2. As observed from the Table 2, 40.4 wt% of oil palm fronds is hemicellulose. The high percentage of hemicellulose is vital in the furfural production since it is produced from the xylose units of xylan in hemicellulose.

The reaction was conducted in a high-pressure and high temperature mini batch reactor made from stainless steel (SS316) as shown in Fig. 1. The reactor consists of 2 bulkhead unions (3/4 in OD) with 15 mL working volume. The mini batch reactor is subsequently placed in a Carbolite ELF 11/1413 muffle furnace. The furnace is equipped with controlled fast heating rate in order to ensure the reaction

| Chemical Component | Chemical Composition (wt%) |
|--------------------|---------------------------|
| Cellulose          | 30.4                      |
| Hemicellulose      | 40.4                      |
| Lignin             | 21.7                      |
| Extractive         | 1.7                       |
| Ash                | 5.8                       |
temperature inside the reactor was achieved rapidly. The reaction time was considered from the moment the furnace reached the targeted reaction temperature. It was determined that the heating rate of the furnace as 24 °C/min from the room temperature. The rapid heating rate ensured that the reaction occurred at the targeted reaction temperature.

The biomass was weighed according to the desired solid loading and transferred into the batch reactor and the liquid (ethanol and formic acid) was pipetted in according to the desired alcohol: acid ratio (w/w). The designated alcohol and acid amount corresponded to the total volume of 15 mL for each run. This was done to ensure the solid biomass was fully immersed in the mixture during the reaction. The reactor was sealed with a single cap SS 316 before placed in the muffle furnace. Finally, the reactor was removed from the muffle furnace and immersed in cold water for instant cooling to room temperature. The liquid-solid mixture was removed from the reactor and filtered by using Syringe Filter, 0.45 µm to separate the solid residue from the liquid product. Furfural was quantified using High Performance Liquid Chromatography (HPLC). Furfural yield (wt%) was calculated based on the equation below.

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\text{Yield (\%)} = \frac{\text{Furfural mass (g)}}{\text{Hemicellulose fraction of oil palm fronds (g)}} \times 100\%
\]

Table 3 shows the experimental conditions of this study. The pressure was kept constant at 35 MPa, above critical pressure of ethanol, while other parameters (solid loading, reaction time, temperature, and alcohol: acid ratio) were varied to examine its effects towards furfural yield.

### Table 3 Experimental condition

| Parameter          | Feedstock |
|--------------------|-----------|
| Pressure (MPa)     | 35        |
| Solid Loading (g)  | 0.4, 0.6, 0.8 |
| Reaction Time (min)| 1, 5, 10  |
| Temperature (°C)   | 240, 260, 280 |
| Alcohol: Acid Ratio(g)| 1:1 and 1:2 |

3. Result and Discussion

The effect of alcohol: acid ratio towards the furfural yield is shown in Fig. 2. In this study, the increase in acid ratio at temperature 240 °C and 280 °C did not significantly affect the furfural yield. On the other hand, for 260 °C, there was significant increase in furfural yield when the alcohol: acid ratio was increased to 1:2 (45.8 % for 1:1 ratio to 88.7% for 1:2 ratio). Therefore, we can conclude that although formation of furfural is promoted by formic acid, its concentration is not an important factor. Antal et al. (1991) in their study of furfural production from D-xylose with sulfuric acid concluded that xylose decomposition is strongly influenced by the acid concentration. Yang et al. (2012) concluded that acid accelerated not only the dehydration of xylose into furfural but also furfural loss reaction. Instead of furfural, the acid hydrolysis of hemicellulose can produce other biomass-derived chemicals such as levulinic acid and hydromethylfurfural. In addition, the furfural loss reaction was significantly enhanced by temperature. Therefore, the minimal change in the furfural yield for different acid ratio at 240°C can be attributed to the low temperature.

The significant increase in furfural yield with acid concentration when the temperature was further increased to 260 °C was consistent with the results obtained previously. Xylose dehydration to produce furfural was significantly enhanced with the increase in acid ratio. The significant increase in furfural yield also implied that the suggested furfural loss reaction due to the increase in acid was not significant at this reaction temperature. On the other hand, the minimal change in the furfural yield at 280 °C despite the increase of acid ratio supported the conclusion by other studies that there was further decomposition of furfural...
to produce other intermediates that caused lower furfural yield \(^{11,12}\). Yang \textit{et al.} (2013) concluded that formic acid concentration is not an important factor in the reaction \(^{12}\). Fig. 3 shows the effect of temperature towards furfural yield at different reaction time (1-10 min). The furfural yield increased with temperature for all reaction time from 240 °C to 260 °C but subsequently decreased when the temperature was further increased to 280°C. For example, the furfural yield increased from 53.8% at 240 °C to 88.7% at 260 °C (10 min). However, it subsequently decreased to 74.9% at 280 °C. As observed from study by Yenis and Mazza (2011), furfural yield is strongly influenced by temperature \(^{17}\). The reduction in furfural yield despite higher temperature can be attributed to the cross-linking and self-polymerisation taking place simultaneously in the reaction \(^{12,17}\). Cross-polymerisation between furfural and the intermediates produced from xylose-to-furfural resulted in the furfural decrease at 280 °C. In addition, the self-polymerisation reaction in which furfural was further polymerized lead to the formation of other intermediates that resulted in the decrease in furfural yield. This observation is consistent with Brand and Kim (2015) \(^{18}\). They suggested that the decrease in furfural yield with temperature was not only caused by the reactions between furfural and the decomposed products but also pyrolytic transformation between these compounds \(^{18}\). Furthermore, the liquefaction in supercritical ethanol appears to have only pyrolytic cleavage as the dominant degradation mechanism. As these pyrolytic reactions were accelerated with temperature, the further degradation of furfural resulted in the decrease of its yield. Brand \textit{et al.} (2014) concluded that the polymerization of the intermediates were retarded at elevated temperatures (> 350 °C) and longer residence times due to hydrogen donation and hydroxyalkylation that stabilized these reaction intermediates and suppressed pyrolytic reactions \(^{19}\). This resulted in high furfural yield. Gairola and Smirnova (2012) suggested that under hydrothermal conditions, furfural undergoes cross-linking with lignin and phenolic resins when biomass was used as the raw material \(^{20}\). It is possible that this is the same reason to the decrease in the furfural yield at higher temperature in this study.

In addition, Fig. 3 also shows the effect of reaction time towards the furfural yield. Based on Fig. 3, the longer reaction time lead to higher yield of furfural. This finding is consistent with other study that observed the increase in furfural yield from xylose decomposition with longer reaction time under similar temperature conditions as used in this study (< 300 °C) \(^{11}\). From the study by Yemis and Mazza (2011) of acid-catalyzed conversion of xylose into furfural using microwave-assisted reaction, they observed the increase in furfural yield when the residence times were increased from 1 to 20 min \(^{17}\). Yang \textit{et al.} (2013) observed that the furfural yield first increased with reaction time from 30 to 60 min \(^{12}\). However, the yields decreased slightly when the reaction time was extended to 200 min. They attributed this to furfural degradation to produce other intermediates.

Fig. 4 shows the effect of solid loading (0.4-0.8 g) towards furfural yield at different reaction temperature. We observed that the increase in solid loading resulted in lower yield of furfural for all temperatures. The effect of solid loading or substrate concentration towards furfural yield has been discussed by several studies. Yemis and Mazza (2011) observed that furfural yield decreased linearly with the substrate concentration for pure xylose \(^{17}\). They attributed the decrease in furfural yield to the increase probability of condensation taking place between furfural and xylose \(^{27}\). Since this study utilized biomass that consisted of cellulose and lignin, besides hemicellulose, there

![Fig. 3 Effect of reaction temperature towards furfural yield at different reaction time (1:2 alcohol:acid ratio, and 0.6 g solid loading)](image)

![Fig. 4 Effect of solid loading towards furfural yield at different temperatures (1:2 alcohol:acid ratio, and 10 min reaction time)](image)
was also possibility of other interactions between furfural and these compounds that resulted in the lower furfural yield with the increase in solid loading.

The highest furfural yield obtained from this study is 88.7% (basis of hemicellulose fraction weight in oil palm fronds) or 35.8% (basis of oil palm fronds dry weight). The results obtained in this study are comparable with other studies done so far. For example, Antal et al. (1991) in their study of D-xylose decomposition in subcritical water with the presence of sulphuric acid at short residence time obtained the highest furfural yield of 64% (250 °C, 34.5 MPa, and 50 s reaction time) 11). On the other hand, study done by Yang et al. (2013) of furfural production from D-xylose with formic acid as catalyst obtained the maximum furfural yield of 74% in 75 min at 190 °C 13). Several studies had been done on furfural production from real biomass. For example, Mao et al. (2012) in their study of furfural production from corn cob through acetic acid catalyzed hydrolysis 21). The maximum furfural yield of 67.9% was obtained at 180 °C with 30 min residence time. The yield was calculated based on the theoretical production of furfural, similar with the basis used in this study. Another study by Suzía et al. (2012) with rice husk to produce furfural using sulfuric acid obtained the highest furfural yield of 8.9% (basis of biomass dry weight) at 177 °C, and reaction time of 4.8 h 22). Wiboon and Poonsuk (2011) obtained the highest furfural yield of 17.34% at 125 °C, and 30 min reaction time with sulfuric acid as catalyst 23). Overall, supercritical ethanol with formic acid as catalyst is proven to be an effective medium for biomass conversion to produce furfural.

4. Conclusion

From this study, the production of furfural from oil palm fronds using supercritical ethanol with formic acid as catalyst is successfully obtained. The highest yield of furfural (88.7%) were obtained at 260 °C, 10 min, with 1:2 alcohol acid ratio, and 0.6 g of solid loading. The reaction temperature, reaction time, and solid loading significantly influenced the furfural yield. On the other hand, although acid is an important catalyst in enhancing the furfural production, its concentration was not an important factor. Overall, supercritical ethanol with formic acid as catalyst is proven to be an effective medium for biomass conversion to produce furfural.

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