Furfural Production from Oil Palm Biomass Using a Biomass-derived Supercritical Ethanol Solvent and Formic Acid Catalyst

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Abstract

This research aimed to produce furfural from oil palm biomass via a biomass-derived solvent (supercritical ethanol) and catalyst (formic acid). The process is 100% biomass-based without the addition of any synthetic chemicals. Ethanol can be produced from biomass through biochemical or thermochemical conversion processes, and formic acid is a by-product of furfural production. Hence, this proposed method is self-sustainable because both can be recycled in the process. Oil palm biomass as a feedstock can address the issue of waste from the palm oil mill industries and turn it into value-added platform chemical such as furfural. In this study, various reaction parameters were evaluated including temperature (240-280°C), reaction time (1-30 min), biomass solid loading (0.4-0.8g), and alcohol: acid ratio (1:1 and 1:2), in a high-pressure and high-temperature batch reactor. The highest furfural yield of 35.8% was obtained in this study, comparable to other commercial and conventional methods. Although the formation of furfural is promoted by formic acid, the reaction temperature significantly impacted the outcome. The significant role of supercritical ethanol as both solvent and reactant may explain the minimal effect of formic acid as a catalyst in the reaction. The high yield of furfural under supercritical ethanol conditions proven in this study illustrates the great potential of this production method.

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1. Introduction

Lignocellulosic biomass has been acknowledged as a realistic alternative bioresource for the production of fuels, various intermediates, and end-product chemicals that are currently derived from non-renewable sources.

The attraction of producing platform chemicals from renewable resources such as biomass has certainly increased with the declining fossil fuel reserves and their increasing price. Cellulose and hemicellulose-derived carbohydrate compounds from biomass can be refined into various value-added products. However, the decomposition/hydrolysis reactions to produce these products are rather challenging due to the high crystallinity of cellulose and the presence of complex lignin polymer networks that formed a sheath of lignin/hemicellulose [1]. Therefore, unravelling the polymer structure of hemicellulose is vital for maximum conversion of the lignocellulosic biomass to platform chemicals.

Furfural has been identified as one of the Top 30 highest value-added bio-based chemicals by the United States Department of Energy in 2004 [2,3]. Furfural, a key compound for the production of various platform and value-added chemical additives can be derived from hemicellulose. Its tremendous potential lies in its value as a competitor with oil derivatives as platform chemicals. It can be used to produce a wide range of non-petroleum derived chemicals such as furan, tetrahydrofuran, and furfuryl alcohol, as well as in areas such as agriculture (herbicides, fungicides, insecticides), food (flavouring agents), medicine (tuberculosis remedies), pharmaceuticals, and plastics, (resins and synthetic fibres) [4]. Furfural is commercially produced through a hydrothermal process using a homogenous acid catalyst that enhances the hydrolysis of hemicellulosic pentosans in the biomass and subsequently the dehydration of the hemicelluloses sugar fragments to produce furfural [5]. In the literature, various types of agricultural residues have been used to produce furfural: olive trees [6], palm pressed fibre [7], birch wood [8], eucalyptus [9], corn cobs [10,11], date-palm trees [12], wheat straw [13], sorghum straw [14], sugar cane bagasse [15], rice husks [16], and rice straw [17]. The versatility of feedstock for furfural production demonstrated its worldwide potential where the choice of feedstocks depends on the geographical availability as well as the policy framework and support by the nation involved.

The vital role of the catalyst in the hydrolysis and dehydration has been previously established. The most widely used process in the industry, the Quaker Oats process, uses sulfuric acid as a catalyst. There are various types of homogenous and heterogeneous catalysts used in furfural production. Homogenous catalysts including mineral acids such as sulfuric acid [12], hydrochloric acid [18], phosphoric acid [14], and nitric acid [19] have been widely reported as efficient catalysts for commercial furfural production. However, these expensive mineral acids catalysts cause the corrosion of pipelines and valves at high temperatures, safety issues, and environmental issues due to hazardous waste effluents. Mineral acids led to undesirable side reactions due to the severe acidity. Therefore, an improvement on the process is needed with the aim to eliminate these complications. Few studies using organic acids to replace mineral acids such as formic acid [13] and acetic acid [15] have been done. Weaker organic acids selectively hydrolyse only the weaker bonds in the hemicellulosic fraction, leaving the cellulose and lignin structures unaltered. In addition, the use of organic acids such as formic acid is an especially attractive and feasible option in an integrated biorefinery because formic acid is one of the by-products during furfural production from the cleavage of the formyl group or the hydrolytic fission of the aldehyde group of furfural. Thus, it is readily available in the process. Formic acid can be recovered from the reaction medium after the reaction via thermal operation, and the waste-producing neutralization of mineral acids can be avoided [20].

Ethanol, a biomass-derived solvent produced from next generation biomass feedstocks through biochemical or thermochemical processes has tremendous potential in furfural production especially under supercritical conditions, as an effective medium in biomass liquefaction [21-24]. The chemical and physical properties of supercritical fluids vary from gas-like to liquid-like by manipulating its temperature and density, which affects its ionic product and dielectric constant has led to increased attention regarding its use as a reaction medium, especially in the gasification and liquefaction of biomass. Ethanol has a critical temperature of 244 °C and critical pressure of 6.38 MPa, considerably lower than other biomass-derived solvents, thereby offering milder conditions for the reaction [25]. Under these conditions, it can dissolve non-polar organic substances. This is extremely advantageous in biomass reactions because supercritical ethanol can readily dissolve and breaks the linkages between lignin and hemicellulose, thus rendering them accessible for acid-catalysed hydrolysis.
To date, there are no studies using oil palm fronds (OPF) to produce furfural, although some studies have used empty fruit bunches (EFB) and palm pressed fibre (PPF) [7,26]. Highest furfural yield of 5.6 wt% were obtained from EFB under hydrothermal conditions with dilute sulfuric acid [26]. Riansa-ngawong and Prasertsan [7] obtained a maximum furfural production of 17.34% from PPF using dilute sulfuric acid. Realizing the challenges in current furfural production, a method that is not only environmental friendly but also chemically feasible should be developed to improve the efficiency. It is vital to extract both the hemicellulose fraction from the confines of the exterior lignin wrapper and the cellulose component interspersed in the framework of the cellulose structure before the hemicellulose fraction is used as the substrate for the production of furfural. Therefore, this study proposed the use of supercritical ethanol to solubilize and break the structural linkages between lignin and hemicellulose from OPF biomass with formic acid as a catalyst for the hydrolysis and dehydration of the xylose to produce furfural.

2. Materials and Methods

2.1. Materials

OPF were obtained from a palm oil plantation in Negeri Sembilan, Malaysia. The raw materials were dried at 45°C for 3 days and cooled down to room temperature. The oven-dried fiber was subsequently ground in a heavy-duty blender until the entire samples passed through 1.0-mm sieve screens to ensure the uniform particles sizes. Total solid and moisture contents of the OPF were conducted based on National Renewable Energy Laboratory (NREL) analytical procedures [27]. The chemical composition of the OPF is also shown in Table 1 [28-31]. From Table 1, 40.4 wt% of the OPF consisted of hemicellulose. This high percentage is vital because furfural is produced from the xylose units of xylan in hemicellulose.

<table>
<thead>
<tr>
<th>Types of Analysis</th>
<th>Percent Content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Solid Content</td>
<td>99.8%</td>
</tr>
<tr>
<td>Total Moisture Content</td>
<td>0.2%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chemical Component</th>
<th>Chemical Composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>30.4</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>40.4</td>
</tr>
<tr>
<td>Lignin</td>
<td>21.7</td>
</tr>
<tr>
<td>Extractive</td>
<td>1.7</td>
</tr>
<tr>
<td>Ash</td>
<td>5.8</td>
</tr>
</tbody>
</table>

2.2. Methods

The reaction was conducted in a mini batch reactor made from stainless steel (SS316) consisting of two bulkhead unions and two caps (3/4-in. OD). The working volume of the mini batch reactor was 15mL. The measured reactants (ethanol and formic acid) and OPF were mixed in the mini batch reactor, and the reactor was sealed tightly before being placed in a Carbolite ELF 11/1413 muffle furnace. The reaction time was considered from the moment the furnace reached the targeted reaction temperature. The reactor was subsequently removed from the muffle furnace and immediately immersed in cold water (24°C) for instant cooling to room temperature. The pressure was maintained at 35 MPa, above the critical pressure of ethanol, while the other parameters (temperature, reaction time, solid loading, and alcohol: acid ratio) were varied to examine their effects on the furfural yield. The product mixture was removed from the reactor and filtered using a 0.45 µm syringe filter, to separate the solid residue from the liquid product. Furfural was quantified on a high-performance liquid chromatograph (HPLC) with a Perkin Elmer series 200-diode array detector. Chromatographic separation was carried out on a Supelcosil™ LC-18 HPLC column (15 cm × 4.6 mm, 5µm) with an acetonitrile and distilled water mixture as the mobile phase. Table 2 shows the experimental conditions of this study.
Table 2. Experimental conditions

<table>
<thead>
<tr>
<th>Types of Condition</th>
<th>Experimental Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (MPa)</td>
<td>35</td>
</tr>
<tr>
<td>Solid Loading (g)</td>
<td>0.4-0.8</td>
</tr>
<tr>
<td>Reaction Time (min)</td>
<td>1-30</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>240-280</td>
</tr>
<tr>
<td>Alcohol: Acid Ratio (g)</td>
<td>1:1 and 1:2</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1. Comparison of the furfural yield

The furfural yields obtained in this study ranged from 4.9 to 35.8% (OPF dry weight basis). The furfural yields obtained from this process were much higher than from other oil palm biomass feedstock [7,26]. A furfural yield of 5.6% was obtained from oil palm EFB under hydrothermal conditions (198 °C and 11 min residence time) with dilute sulfuric acid [26]. Riansa-ngawong and Prasertsan [7] obtained 17.34% with oil palm pressed fiber using dilute sulfuric acid. This shows the potential of using biomass-derived supercritical alcohol as a reaction medium with formic acid as a catalyst for furfural production.

A comparison of the optimum furfural yields obtained from other studies using different biomass feedstocks over a similar temperature range as the present study is shown below in Fig. 1. The yield obtained in the present study was comparable to that of Lin et al. [17] and Montané et al. [32] with a similar reaction temperature range. However, the yields were lower compared to other studies [12, 33,34]. The difference in these furfural yields could be attributed to several factors, such as the different types of biomass feedstock resulting in different xylose contents, types of catalyst, reaction conditions, and reaction media. Some of the reported studies (Fig. 1) used mineral acids as catalyst in the reaction, which resulted in higher yield. However, furfural yield from this study is compatible with few other studies. This shows that by combining supercritical alcohol with organic acid, comparable furfural yield can be obtained. Nevertheless, this comparison shows that supercritical alcohol with formic acid is feasible as a reaction medium and catalyst for furfural production from biomass.

![Fig. 1. Comparison of furfural yield with other studies using different biomass feedstocks](image)

3.2. Effect of the reaction temperature

The furfural yield is significantly influenced by temperature because it is a crucial factor in all thermochemical processes [35]. Fig. 2 shows the effect of reaction temperature on furfural yield at different reaction times. Higher temperature resulted in an increase of the furfural yield at short reaction times (1-10 min). However, the effect of
temperature was not significant at longer reaction times (20-30 min). This is an interesting observation that indicates reaction time is just as important as temperature for this reaction under supercritical conditions. Riansa-ngawong and Prasertsan [7] similarly observed the profound effect of temperature and reaction time on furfural production. They concluded that the furfural yield increased either with increasing reaction temperature and shorter reaction time or with decreasing reaction temperature and longer reaction time.

![Fig. 2. Effects of reaction temperature (240-280 °C) towards furfural yield at different reaction time: (a) 1:1 alcohol:acid ratio, and 0.4 g solid loading; (b) 1:2 alcohol:acid ratio, and 0.8 g solid loading](image)

The increase in reaction temperature accelerates the depolymerization of the linkages between the carbon bonds of pentosan as well as the dehydration of xylose to furfural. Supercritical ethanol further enhances the dehydration of xylose to produce furfural because it readily dissolves and breaks the linkages between lignin and hemicelluloses through pyrolytic cleavage as the dominant degradation mechanism [24]. Pyrolytic cleavage was the dominant degradation mechanism in the reaction and was significantly enhanced by temperature. Clearly, this mechanism has faster formation kinetics, resulting in an increase in furfural formation with temperature at short reaction times. However, a high reaction temperature may enhance another competitive mechanism, mainly the formation of other liquid and/or solid products through repolymerization, condensation, and cyclization of the intermediates that consumed the liquid products including furfural [21]. The decrease in the furfural yield with temperature was caused not only by the reactions between furfural and the decomposed products but also by pyrolytic transformation between these compounds [24]. Because the low furfural yields were only observed at longer reaction times in this study, we can deduce that this reaction occurred at a slower rate and that its impact was only significant at prolonged reaction times. Raman and Gnansounou [26] discovered the formation of a dark solid precipitate believed to be humin at a high temperature and long reaction time and concluded that all of xylose in the biomass and a significant portion of furfural were converted to humin at extreme temperatures and long reaction times.

In our study, this solid formation was only observed at 30 min. This was consistent with Brand et al. [22] conclusion that supercritical ethanol acts as a hydrogen donor, which may suppress active reaction intermediates species and consequently retard the condensation and cracking reactions that contribute to humin formation. Supercritical ethanol as an organic solvent enhanced the decomposition, depolymerized the biomass to fragments of lighter molecules, and simultaneously prevented these unstable fragments from condensing and polymerizing to form undesirable solid products [21,37].

### 3.3. Effect of the reaction time

Fig. 2 previously shows the effect of reaction time as well as temperature on the furfural yield. There was a similar trend in the yield with reaction time at all temperatures. Initially, there was a significant increase in the furfural yield during the first 20 min before it decreased when the reaction time was extended to 30 min. There are two phases in the furfural formation, the aqueous phase and extractive phase, and both of these phases occur in the homogeneous media.
(liquid-liquid equilibrium) [38]. The increase in the initial furfural formation (1-20 min) is due to the high availability of xylose in the biomass. As the reaction progressed, the furfurals produced were continuously removed into the organic phase of ethanol, while xylose/xylan, the hydrophilic intermediates and degradation products, were in aqueous phase. As the reaction time was prolonged, the furfural concentration in the organic phase eventually achieved its maximum achieved concentration. At 30 min, this resulted in the acceleration of the subsequent rate of furfural loss, becoming much faster than its initial rate of formation. The furfural-loss reactions, such as the condensation and self-polymerization of furfural (resinification) and cross-polymerization with other degradation products (i.e., lignin-like material, especially phenolic compounds) or with the intermediates of xylose conversion, have been discussed extensively and are the cause of the low furfural yield at long reaction times [11,39].

3.4. Effect of alcohol: acid ratio

The effect of the alcohol: acid ratio on the furfural yield is shown in Fig. 3. In this study, the increase in the alcohol: acid ratio from 1:1 to 1:2 resulted in an increase in furfural yield. There was a significant increase in the furfural yield when the alcohol: acid ratio was increased from 1:1 to 1:2 at lower temperatures (240 °C and 260 °C), but there was only a minimal increase in the yield at a higher temperature (280 °C). Thus, we can conclude that, although formation of furfural is promoted by formic acid, the reaction temperature significantly impacts the outcome.

![Figure 3](image.png)

Fig. 3. Effects of alcohol:acid ratio (1:1 and 1:2) towards furfural yield at different reaction temperature: (a) 10 min reaction time, and 0.4 g solid loading; (b) 5 min reaction time, and 0.6 g solid loading

This phenomenon can be explained by investigating the mechanism. The increase in reaction temperature especially above the critical conditions caused a significant decrease in the dielectric constant in the reaction medium. This in turn decreased the hydrogen ion concentration of the formic acid, which may completely dissociate at higher temperatures. Therefore, the effect of formic acid concentration on the reaction rate and furfural formation was diminished, and it was likely supercritical ethanol that played a more significant role in the reaction. Yang et al. [38] further concluded that formic acid not only accelerated the dehydration of xylose to produce furfural but also accelerated the furfural loss reactions. It is equally important to determine the role of supercritical ethanol as the reaction medium. Ethanol under ambient conditions has a dielectric constant of approximately 25. However, this decreases significantly to below 4 under supercritical conditions [22]. The significant decrease in the dielectric constant resulted in the important role of supercritical ethanol as an excellent hydrogen donor. Hydrogen generated from supercritical ethanol can undergo hydrogenolysis, facilitating depolymerization in the biomass, especially in the weaker hemicellulose fractions [22]. In addition, due to the lower dielectric constant, free radical generation was enhanced, which can facilitate the quenching and retardation of repolymerization and the formation of solid product. This resulted in more liquid products such as furfural. The significant roles of supercritical ethanol as both solvent and reactant may explain the minimal effect of formic acid as a catalyst in the reaction.
3.5. Effect of solid loading

Fig. 4 shows the effect of solid loading (0.4–0.8 g) on the furfural yield at different temperatures. The increase in solid loading resulted in significantly lower furfural yields at all temperatures.

![Graphs showing furfural yield at different temperatures with varying solid loadings](image)

Yemis and Mazza [13] attributed the decrease in furfural yield to solid loading due to the increased probability of condensation occurring between furfural and xylose. It has been established previously that furfural loss reactions, which include resinification and condensation, occur not only between furfural but also with other intermediates and fragments in the biomass, which would decrease the furfural yield. These undesirable side reactions between furfural and its precursors were possibly enhanced due to a higher solid loading. You et al. [40] also observed that the selectivity of the decomposition products showed a stronger dependency on the xylose concentration. They further concluded that an increase in xylose concentration resulted in a significant increase in humin selectivity.

4. Conclusions

In this study, the production of furfural from OPF using supercritical ethanol with formic acid as a catalyst was successfully demonstrated. The highest furfural yield of 35.8% was obtained in this study, comparable to other commercial and conventional method. From this study, it can be concluded that higher reaction temperature and acid concentration with moderate reaction time as well as low amount of solid loading enhanced the furfural yield. Supercritical ethanol was able to enhance the decomposition and depolymerization of xylose in biomass to yield liquid products such as furfural and simultaneously prevent these unstable fragments from condensing and polymerizing to form undesirable solid products. Formic acid was able to accelerate the selective hydrolysis of only the hemicellulose fraction in the biomass. Although the formation of furfural is promoted by formic acid, the reaction temperature significantly impacts the outcome. The significant role of supercritical ethanol as both solvent and reactant may explain the minimal effect of formic acid as a catalyst in the reaction. The high yield of furfural under supercritical ethanol conditions proven in this study illustrates the great potential of this production method.

References