Furfural Production Under Subcritical Alcohol Conditions:
Effect of Reaction Temperature, Time, and Types of Alcohol

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Oil palm fronds (OPF) are potential resources for production of biomass-based chemicals such as furfural, levulinic acid, and 5-HMF due to its large abundance. Although there are various conventional methods for biomass conversion, they suffer from low yields as well as extreme reaction severity due to the usage of mineral acids as catalyst. A new method using subcritical alcohol can be an alternative. Hence, the aim of this study is to determine the feasibility of using subcritical alcohol for furfural production from OPF. The study will also determine the effect of reaction parameters such as reaction temperature, time, and types of alcohol towards the yield. From the study, it is concluded that high furfural yield can be achieved at milder temperature and moderate reaction time under subcritical conditions. The yield obtained is comparable with other conventional methods indicating that subcritical alcohol technology has the potential for furfural production.

Key Words
Furfural, Oil palm biomass, Subcritical alcohol

1. Introduction

The exponential development of palm oil industries in Malaysia starting from early 1960s until present has been largely attributed to various government efforts by constituting several systematic estates such as Federal Land Development Authority (FELDA), Federal Land Consolidation and Rehabilitation Authority (FELCRA). According to Malaysian Palm Oil Council (MPOC) statistic, crude palm oil production has increased to 19.8 million tons in 2015 due to global demand of palm oil in various industries (food, oleo-chemical, and energy). Consequently, Malaysia has generated excessive amount of agricultural residues from oil palm plantation with 86 million tons of dry weight biomass in 2010 and it is estimated to reach 100 million tons by 2020. The most abundant biomass generated from oil palm plantations are oil palm trunks (OPT), OPF, empty fruit bunches (EFB), palm kernel shells (PKS), and palm pressed fibres (PPF). 10.88 tons of OPF are produced for each hectare of oil palm plantation.

OPF is generally constituted of 30.4 wt% cellulose, 40.4 wt% hemicellulose, and the rest are lignin and extractives. However, the biggest challenge in the conversion of lignocellulosic biomass is due to the complex polymer structure whereas a sufficient pre-treatment is needed to break down the biomass structure, eliminating the lignin content, increasing the surface area, and reducing the crystalline of cellulose. Therefore, it is vital to unravel these polymer structures for maximum conversion of biomass to valuable chemical products.

Biomass liquefaction under sub- and supercritical conditions has been extensively reported as one of the
alternative processes. Common green solvent used in biomass liquefaction is water since it is readily available, cheap, and non-toxic. However, its extreme condition (TC = 374 °C, PC = 221 MPa) is a major challenge. Hence, new approach using alcohol gains interest as replacement to water. Critical points of ethanol (TC = 244 °C, PC = 6.68 MPa) and methanol (TC = 239 °C, PC = 8.09 MPa) are much lower compared to water. The unique properties of alcohol as solvent with its liquid-like density enhances the solubility of non-polar organic substances, eliminates the complexity of many chemical syntheses, and offers milder reaction conditions with more accessible critical properties, offering an alternative medium of reaction to overcome the complications associated with sub- and supercritical water.

Although the feasibility of using sub- and supercritical alcohol towards biomass conversion to bio-based chemicals has been established, there is very few attempted studies to determine and compare the effect of these alcohols as reaction medium towards furfural production from biomass.

In our previous studies, we established the existence of competitive mechanisms during the reaction. Initially, high temperature accelerates the depolymerization of the linkages between the carbon bonds of pentosan as well as the dehydration of xylose to furfural through pyrolytic cleavage as the dominant degradation mechanism. This mechanism has faster formation kinetics, resulting in an increase in furfural yield with temperature at short reaction times. However, higher temperature enhanced 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. This resulted in the formation of dark solid precipitate believed to be humin.

In this study, we focused on the feasibility of using lower reaction temperature. We proposed the usage of two types of subcritical alcohol (ethanol and methanol). Different types of alcohol will influence the product yield due to the changes in its dielectric constant, which increases the solubility and diffusivity of many compounds in the reaction media. At ambient temperature, ethanol and methanol has dielectric constant of 25.02 and 33.15, respectively. Dielectric constant is largely determined by the size of alkyl chain of the alcohol. Longer alkyl chain results in lower value of dielectric constant. Therefore, the main purpose of this study is to do comparison on the effects of different alcohol solvent (methanol and ethanol) towards the reaction. In addition, the effects of reaction temperature and time towards furfural yield under these conditions are also investigated.

### 2. Experimental

#### 2.1 Raw Materials and Chemicals

OFF was obtained from FELDA plantation in Negeri Sembilan, Malaysia. The dried biomass samples were initially grinded before sieved to obtain uniform particle size. Prior to experiment, the biomass samples were dried in oven at 105 °C for 12 h to remove any residual moisture. Methanol and ethanol (analytical grade) from R&M Chemicals (United Kingdom) were used in this study. The reference standard for Furfural (analytical grade) was obtained from Sigma Aldrich (Honeywell Specialty Chemicals, Malaysia). Meanwhile, Acetonitrile (HPLC grade) from R&M Chemicals were used for analysis purposes.

#### 2.2 Method and Analysis

The reaction was conducted in a mini batch reactor made from stainless steel (SS316) consisting of two Swagelok bulkhead unions (19.05 mm OD) and capped with two SS316 Swagelok cap (19.05 mm OD). The reactor has a working volume of 30 mL equipped with temperature gauge for accurate measurement of the internal reactor temperature. The measured solvent (ethanol or methanol) and OPF samples were weighed before placed in the mini batch reactor and subsequently sealed. The reactor is subsequently immersed in Digital High Temperature Oil Bath (WHB-6L) with glycerol as heating medium.

The reaction time was considered from the moment the reactor reached the targeted reaction temperature. After the reaction completed, the reactor was immersed immediately in the water bath for instant cooling to room temperature to quench any undesirable reactions. The liquid product was separated from its solid residue. Furfural quantification was performed using Shimadzu LC-20AP Low Gradient System array detector high-performance liquid chromatography (HPLC) with C18 SupelcosilTM HPLC column (15 cm × 4.6 mm, 5 μm). A mixture of acetonitrile and distilled water (90:10 v/v) was used as the mobile phase. Furfural yield was calculated based on the equation below.

\[
\text{Furfural Yield [%]} = \frac{\text{Furfural mass (g)}}{\text{Hemicellulose Content (g)}} \times 100\%
\]

Reaction temperature, reaction time and different types of solvents were varied to study their effects on the falls. The following table shows the parameters used in the experiment.

<table>
<thead>
<tr>
<th>Types of Condition</th>
<th>Experimental Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (MPa)</td>
<td>9</td>
</tr>
<tr>
<td>Time (min)</td>
<td>0.5 - 30</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>100 - 230</td>
</tr>
<tr>
<td>Solvent</td>
<td>Ethanol or Methanol</td>
</tr>
</tbody>
</table>

**Table 1 Experimental conditions**
furifural yield at fixed pressure of 9 MPa. Table 1 shows the experimental conditions of this study.

3. Results and Discussion

3.1 Effect of Temperature

Thermal liquefaction is a chemical reaction in which the complex matrix between the structural frameworks of plant is broken down at certain range of temperatures. In our study, two types of alcohol (methanol and ethanol) were used at different temperatures (100 °C – 230 °C) under sub-critical conditions. In any thermochemical processes, the most significant parameter towards the reaction is temperature. Fig. 1 (a) and (b) shows the effect of temperature towards furfural yield for different types of alcohol.

Both Fig. 1 (a) and (b) demonstrated similar trend. Higher reaction temperature enhanced the furfural yield. At 100 °C, the furfural yields obtained were 0.2-12% respectively for ethanol and methanol. Although the yield is relatively minimal, this indicated furfural could be obtained at low reaction temperature under subcritical conditions. Meanwhile, the highest furfural yields obtained at 230 °C were 41.34% and 32.70% for ethanol and methanol respectively.

Hemicellulose in biomass functioned as linkers between cellulose, micro fibrils, and lignin. These linkages created strong bonds between the matrix network contributing to its structural stability. 21) 22) Higher temperature is needed to break the linkages between these complex structures. It has been suggested that conversion of xylose, a sugar-monomer to furfural were enhanced only at temperatures higher than 140 °C 21) 23). This is consistent with the results shown here, less than 10% of furfural yield was obtained at 100 °C.

Theoretically, temperature enhanced kinetic energy attributed to the faster movement of molecules. Thus, it increases the molecules movement, and the ability of alcohol under subcritical conditions to readily dissolve and to break the linkages between the carbohydrates, resulting in higher furfural yield at 230 °C. Besides, the lower dielectric constant for higher temperature decreased the polarity of solvents. Therefore, a more compatible reaction medium for both polar and non-polar substances could be obtained which resulted in higher furfural yield. This is in agreement with a few studies that concluded furfural yield is enhanced with high temperature 24) 25). However, these studies also highlighted the degradation of furfural at high temperature resulting in the formation of undesirable humin and char 22) 26) ~ 30). Humin and char were produced through resinification and other competitive mechanism such as repolymerization, condensation, and cyclization of the intermediates during the reaction 31).

3.2 Effect of Reaction Time

The effect of reaction times towards the furfural yield at different temperatures is shown in Fig. 2 (a) and (b) for ethanol and methanol respectively. Based on the figures, longer reaction time significantly increased the furfural yield for the first 20 min but subsequently decreased at longer reaction time (30 min). The increase in furfural formation initially can be attributed to the high accessibility of xylose in the biomass. On the other hand, the subsequent decrease in furfural yield at 30 min can be attributed to side reactions i.e. condensation and resinification 26).

Weingarten et al. (2010) 32) in their kinetic study of
xylose decomposition to furfural, concluded that furfural undergoes two parallel reactions: dehydration process from xylose to furfural, and formation of other decomposition products from reactions between furfural and xylose. They further concluded that the cause of the furfural degradation is due to the second reaction and longer reaction time enhanced this side reaction. Xylose dehydration to furfural occurred at higher rate while rate of furfural degradation was found to be relatively slow. They also constituted the furfural distribution was solely dependent on the bidirectional mass transfer rates (xylose to furfural) and thermodynamic instability did not influence any kinetics or paths. This similar finding is in agreement with studies by Agirrezabal-Telleria et al. (2011) and Dussan et al. (2013). It was also suggested by Williams and Dunlop that longer reaction time caused hydrolytic fission of the furfural aldehydes group.

In pure aqueous solution, xylose conversion to furfural is not favoured at longer reactions time. This is caused by the fact that the rate of furfural conversion to its derivatives known as resification and condensation is higher than that of xylose to furfural. In resification, furfural will undergo self-depolymerisation resulting in the decrease of its yield with longer reaction time. Meanwhile, in condensation process, furfural reacted with other intermediates product (formaldehyde, formic acid, acetaldehyde, crotonaldehyde, lactic acid, dihydroxyacetone, glyceraldehyde, pyruvaldehyde, acetal and glycoaldehyde). From these intermediate reactions, furfural pentose and di-furfural xylose are produced causing the decrease in furfural yield. Although several studies claimed that the effect of reaction time is less significant compared with temperature, it is found in this study that reaction time affected the yield of furfural.

3.3 Effect of Types of Subcritical Alcohol

The usage of high temperature and pressure in supercritical water technology becomes a barrier due to the severity of the reaction conditions. Subcritical alcohol can be ideal replacement since it possesses similar properties but at more accessible temperature and pressure and inherently high tunability tailored to the reactions. Most of studies focused on supercritical alcohol technology and only few studies on the near-critical region. There is current limitation in the knowledge of furfural production near-critical area and the suitability of alcohols as a reaction medium. Fig. 3(a) and (b) illustrated the finding.

Fig. 2 Effect of reaction time (0.5-30 min) towards furfural yield at different reaction temperature: (a) Ethanol and 1g solid loading, (b) Methanol and 1g solid loading

The difference in furfural yield obtained from different types of biomass could be attributed to the difference in xylose content. In addition, the ability of the reaction medium to readily access the sugar monomers and break the linkages between complex compounds, is another factor to be considered. Based on the result shown in Fig. 3(a) and (b), higher furfural yields were obtained with subcritical ethanol compared to subcritical methanol for all temperatures except for 100°C.

Similar studies by Koll et al. (1979) and Yamazaki et al. (2006) reported that conversion of carbohydrates and lignin were enhanced with subcritical ethanol. Studies using supercritical methanol for woody biomass liquefaction determined that longer reaction time (30 min), high temperature, and pressure were needed to achieve high yield of liquid products. Therefore, we concluded that the low furfural yield obtained in this study could be attributed to the moderate reaction temperature and low pressure. Using subcritical alcohol, the reactions are
dominantly ionic instead of free radical, which inhibited furfural degradation and char formation. This is in agreement with studies by Yong and Matsumura \(^{45}\) and Peleteiro \textit{et al.} \(^{46}\). Hua \textit{et al.} \(^{47}\) similarly concluded that furfural yield is attributed to the high value of ionic product (Kw) of the reaction medium indicating the significance of ionic reaction under subcritical conditions.

Ethanol has a higher dissolving power than methanol due to the longer alkyl chains and the extra carbon atom contained in ethanol slightly increases the heat content \(^{48, 49}\). According to Letcher (2007) \(^{50}\), the size of the alkyl chain can affect the solubility of the solvent where the solubility increases with alkyl chain length at all pressure. Increase in dissolving power resulted in higher intermolecular attraction between solvent’ and solute’ molecules hence larger dissociation of hemicellulose compound from complex lignocellulosic biomass. Furthermore, the increase in the heat content consequently increases the size of solubility window of the solvent, due to the increase in entropy during the heating process. It is believed that the strength of the covalent bond of the complex polymer compounds is reduced with larger solubility window. This resulted in depolymerization of biomass to form sugar monomers such as xylose before converted to furfural.

At ambient condition, methanol has high solubility, reactivity, and polarity as well as higher dielectric constant compared to ethanol. However, ethanol possess a unique ability to trigger and enhanced the thermal reaction to behave under subcritical condition.

On the other hand, subcritical ethanol has a high tunability which can influenced the reaction’s phase behaviour, equilibrium state, reaction rate, and also the reaction selectivity \(^{40}\). With these properties, it is believed that subcritical ethanol enhanced biomass liquefaction, with more hemicellulose fraction cleaved and subsequently converted to furfural. On the other hand, as the temperature increases, the decrease in the polarizing ability of subcritical ethanol resulted in decreasing of hydrogen-bond acidity and basicity, similar to a non-polar solvent \(^{51}\). In this condition, subcritical ethanol can be considered as a good hydrogen-bond donor, an effective solvent in any conventional reaction with less corrosive and more reactive compared to subcritical methanol.

![Fig. 3 Effect of different types of alcohol towards furfural yield at different temperature: (a) 1 g solid loading and 10 min, (b) 1 g solid loading and 30 min](image)

4. Conclusion

The production of furfural under subcritical alcohols from OPF was achieved in this study with highest furfural yield of 30%. It is concluded that the production of furfural from OPF is affected by reaction temperature, time, and types of alcohol. Ethanol is more effective in this reaction compared to methanol. The high potential of furfural production from subcritical alcohol at milder reaction temperature and pressure are demonstrated in this study.

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