Assessment of Oil Palm Trunk Liquefaction in Glycerol and Ethylene Glycol by 2⁴⁻¹ Fractional Factorial Design

Mohd Fahmi AWALLUDIN, Othman SULAIMAN†, Rokiah HASHIM, and Mohd Firdaus YHAYA

(Received November 15, 2016)

Liquefaction of oil palm trunk (OPT) in ethylene glycol and glycerol, with H2SO4 as a catalyst, at a temperature of 150 °C was conducted based on Design of Experiment (DoE) aided by software Stat-Ease Inc., Design-Expert® Version 7. A 2⁴⁻¹ fractional factorial design was used. The results showed that factors such as types of solvents, percentage of H2SO4 catalyst and liquefaction time influenced the final liquefaction yield. Liquefaction of OPT in glycerol gave higher amount of liquefied yield. Besides, higher percentage of H2SO4 catalyst and longer liquefaction time also gave higher liquefaction yields.

Key Words
Oil palm trunk, Liquefaction, Design of experiment

1. Introduction

Researchers around the world have studied liquefaction of biomass from forest and agricultural wastes and other lignocellulose products. Among the tree species studied were Japanese beech (Fagus crenata Blume) ¹, poplar (Populus ssp.), alder (Alnus ssp.), linden (Tilia ssp.) and chestnut wood (Castanea sativa Mill.) ² and Chinese tallow (Triadica sebifera syn. Sapium sebiferum) ³. In terms of agricultural crops, among the wastes studied were corn stover ⁴, corn bran ⁵, bagasse and cotton stalks ⁶, moso bamboo (Phyllostachys angusta) ⁷, grapevine cane (Vitis vinisera L.) ⁸ and oil palm (Elaeis guineensis) empty fruit bunch (EFB) ⁹. Other studies involving lignocellulose products were cotton wool and filter paper ¹⁰ and waste paper ¹¹.

There are various uses of liquefied biomass. Among the applications that have been tried and evaluated include resol‐type phenolic resin used in phenolic foam ¹², novolak phenol formaldehyde resin ¹³, liquefied wood/polyurethane films ¹⁴, resin for moulding ¹⁵, wood ceramics ¹⁶, carbon fibres ¹⁷ ¹⁸, liquefied wood/epoxy resin ¹⁹, polymer composites ²⁰, mesoporous activated carbon fibre ²¹ and fuel for gas turbines ²².

For years, Malaysia has strengthening its palm oil industry as a vital source of national income. Malaysian palm oil industry provides a continuous supply of biomass material in the form of agricultural wastes. There were several studies about liquefaction of oil palm wastes such as EFB fibres, mesocarp fibres and palm kernel shells used for phenolated EFB resin and as bio oil ²³ ²⁴. To our knowledge, no liquefaction of waste oil palm trunk (OPT) ever attempted by any researcher. Therefore, we take this opportunity to study the liquefaction of waste OPT in ethylene glycol and glycerol.

The study conducted was based on Design of Experiment (DoE), 2⁴⁻¹ fractional factorial design. This design is useful for estimating linear model terms, where each factor was varied over two levels; highest or lowest values. Besides, this design also enables to find the possible significant variables for the experiment as well as estimating main effects and interactions among factors ²⁵.

2. Experimental

2.1 Materials

A 25 year-old felled OPT during replanting work was procured from an oil palm plantation in Ara Kuda, Kedah, Malaysia. The catalyst used for liquefaction process was sulfuric acid (H2SO4) with 95-97% purity grade. Previous studies suggest that H2SO4 in the range of 1-5 wt% is the best catalyst for biomass liquefaction compared to hydrochloric and phosphoric acids. At higher concentration,

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Technical Report

Special articles: Asian Conference on Biomass Science

Division of Bioresource, Paper and Coatings Technology, School of Industrial Technology, Universiti Sains Malaysia 11800 Minden, Penang, Malaysia

† Corresponding author: fahmi7117@gmail.com
secondary reaction may occur due to strong oxidation effect of H₂SO₄. Two types of liquefying solvents used were reagent grade glycerol and ethylene glycol brand of Sigma-Aldrich. Both solvents are commonly used in biomass liquefaction. Ethanol was used to wash the liquefied OPT yield.

2.2 Feedstock preparation

Five OPT discs were cut out from the middle part of the trunk. Debarked OPT discs were then endured a further downsizing process using a band saw and a chipper. Air dried OPT chips were ground and screened to specific sizes in between 250 and 1000 µm and were further oven dried for 24 hours before it was used as feedstock.

2.3 Oil palm trunk liquefaction

The OPT liquefaction in this study implemented the DoE methodology with aid from software by Stat-Ease, Inc. Design-Expert® Version 7 (Minneapolis, USA). The experimental design adopted a 2⁴⁻¹ fractional factorial design. Four independent variables were selected to be studied that were OPT loading, time, the percentage of catalyst and liquefaction solvents. These variables have been among widely studied by other researchers in biomass liquefaction.

The OPT feedstock, liquefaction solvent and catalyst (H₂SO₄) were mixed according to the formula ratio as described in Section 2.4. The liquefaction reaction was carried out in a 500 ml four-neck glass flask, equipped with an automatic stirrer, a heating mantle, a reflux condenser and an automated temperature probe. The mixture of liquefaction solvent and catalyst was heated first until it reached 150 °C before the OPT feedstock was added. The reaction time was recorded after all of the OPT feedstock was completely added into the reaction flask. When the reaction was finished, the flask that contained a dark brown mixture (liquefied OPT) was immersed in an ice bath to stop the reaction. The excessive amount of catalyst was neutralized with an equivalent sodium hydroxide (NaOH) aqueous solution. The liquefied OPT was then diluted with excessive amount of ethanol and stirred continuously for 5 min with a magnetic stirrer. The solid residue of unliquefied OPT feedstock was obtained by vacuum-filtration using filter paper. It was then rinsed using ethanol until colourless filtrate was obtained and oven dried overnight at 105 °C.

The following Eq (1) calculated the liquefaction yield:

\[
\text{Liquefaction yield (\%)} = \left(1 - \frac{\text{Weight of solid residue (OD)}}{\text{Weight of OPT feedstock (OD)}}\right) \times 100
\]

2.4 Experimental design (DoE): 2⁴⁻¹ fractional factorial design

The liquefaction experiment was carried out based on 2⁴⁻¹ fractional factorial design to study the most significant variables that influence the efficacy of OPT liquefaction. The overall process was simplified according to the chart in Fig. 1. The four liquefaction factors were OPT loading (A), liquefaction time (B), percentage of H₂SO₄ catalyst (C) and liquefaction solvents (D).

The OPT loading is the amount of OPT feedstock added into the liquefaction solvents (w/w). It was coded as -1 and 1 that equals to 30 and 60 g of OPT feedstock in 300 g liquefaction solvent respectively. The minimum liquefaction time was 10 min while the maximum was 120 min. The catalyst percentage was calculated as the weight ratio to liquefaction solvent mass (w/w %). The lowest value was 2%, while the highest was 6%. The liquefaction solvents used were glycerol and ethylene glycol. The low limit value of the solvent that is 0, meaning that 100% glycerol was used as liquefaction solvent and no ethylene glycol presented while at 100 high limit value meaning that 100% ethylene glycol was used with no glycerol presented. The summary of the variables involved is shown in Table 1.

Based on fractional factorial designs (2⁴⁻¹), the number of runs generated were eight (16/2 = 8 runs) but each run was duplicated for more precise estimation. Total number of runs was 16. The number of runs, actual and coded values of independent variables is shown in Table 2.

3. Results and Discussion

3.1 Effect of multiple variable conditions to the OPT liquefaction

The amount of liquefied OPT yield obtained as a response to the different conditions of OPT loading (A), liquefaction time (B), catalyst (C) and liquefaction solvent (D)

![Fig. 1 The experimental design's flow chart for preliminary OPT liquefaction study](image-url)
The final response (liquefied OPT yields) ranges from 51.36% (min) to 81.76% (max). In statistics, generally if the ratio of maximum to minimum value of the response exceeds 10, transformation such as square root, natural log, power and so forth is needed. The calculated ratio between maximum to minimum yield was less than 10, which was 1.59. Therefore, no transformation is needed. The predicted OPT liquefied yields were calculated by the statistical software. It was found that the predicted yield values were in the acceptable range with the experimental value.

### 3.2 Evaluation of the significance factor and interaction

The half-normal plot graphically and statistically categorizes factors (variables) and interactions into important and unimportant group. As can be seen in Fig. 2, the half-normal plot quantitatively estimates the effect of a given primary effect and the interactions relative to the primary effect of the generated model in DoE. The plot ranked the factor/interaction importance according to the farthest to right as most important. The closer to the zero value the least important the factor/interaction is.

The Pareto chart depicted in Fig. 3 was further visualized the importance of each factors and some interactions. In this case, the coefficient of variables with t-value of effect above the Bonferroni limit (t-value of
effect = 3.58) are labelled as indeed significant coefficients. It seems that time (B), solvent (D), catalyst (C) and the interaction factor for AD and AB were found to be statistically significant. Obviously, the effect magnitude by liquefaction time (B) with a t-value of 13.98 has the most significant impact on the OPT liquefaction yields. The coefficient of OPT loading (A) and OPT loading/catalyst (AC) interaction that situated in between t-value limit (t-value of effect = 2.31) and Bonferroni limit was likely less significant. The possible interactions between AB and AD for each response were also investigated as shown in Fig. 4. Graphically, the significance interaction between factors can be interpreted by the lack of parallelism in lines 35. The lack of parallelism in the lines in interaction of the OPT loading (A) to the liquefaction solvents (D), compared to the interaction of OPT loading (A) to the liquefaction time implies that AD interaction is more significant compared to AB interaction.

### 3.3 Analysis of variance (ANOVA)

The analysis of variance (ANOVA) of the model in this study is presented in Table 4. It shows the reliability and the significance of the model generated by the statistical software, alongside with the variables involved. The F-value for the model is of 61.97 indicates that the model is significant. With the “Model F-Value” this large,

**Table 4 Analysis of variance (ANOVA) for OPT liquefaction model**

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F Value</th>
<th>p-value Prob &gt; F</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>1018.38</td>
<td>7</td>
<td>145.48</td>
<td>61.97</td>
<td>&lt; 0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>A (OPT Loading)</td>
<td>18.90</td>
<td>1</td>
<td>18.90</td>
<td>8.05</td>
<td>0.0219</td>
<td></td>
</tr>
<tr>
<td>B (Time)</td>
<td>458.61</td>
<td>1</td>
<td>458.61</td>
<td>195.33</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>C (Catalyst)</td>
<td>130.27</td>
<td>1</td>
<td>130.27</td>
<td>55.49</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>D (Solvent)</td>
<td>163.87</td>
<td>1</td>
<td>163.87</td>
<td>69.80</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>AB</td>
<td>52.59</td>
<td>1</td>
<td>52.59</td>
<td>22.40</td>
<td>0.0015</td>
<td></td>
</tr>
<tr>
<td>AC</td>
<td>24.73</td>
<td>1</td>
<td>24.73</td>
<td>10.53</td>
<td>0.0118</td>
<td></td>
</tr>
<tr>
<td>AD</td>
<td>169.40</td>
<td>1</td>
<td>169.40</td>
<td>72.15</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>Pure Error</td>
<td>18.78</td>
<td>8</td>
<td>2.35</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>1037.16</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>1.53</td>
<td></td>
<td>(R²) R-Squared</td>
<td>0.9819</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>61.76</td>
<td></td>
<td>(R²_adj) Adj R-Squared</td>
<td>0.9660</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CV. %</td>
<td>2.48</td>
<td></td>
<td>(R²_pred) Pred R-Squared</td>
<td>0.9276</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PRESS</td>
<td>75.13</td>
<td></td>
<td>Adequate Precision</td>
<td>25.143</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
there is only a 0.01% chance that it could occur due to noise. The model terms were selected or excluded based on the p-value with 95% confidence level. The p-value for the model, factors (A, B, C and D) or their interactions (AB, AC and AD) are less than 0.05 implies that the terms are significant. The predicted $R^2$ (Pred R-Squared of 0.9276) is in reasonable agreement with the adjusted $R^2$ (Adj R-Squared of 0.9660), which is good. The adequate precision (Adeq Precision) statistically calculates the signal to noise ratio. A ratio greater than 4 is desirable. The adequate precision of 25.143 obtained from the experiment indicates an adequate signal. This model can be used to navigate the design space.

The final empirical models in terms of actual factors for percentage of liquefied OPT yield ($y$) is shown in Eq. (2).

$$y = 52.06 + 0.02A + 0.2B + 3.30C - 0.26D - (2.20 \times 10^{-3})AB - 0.04AC + (4.34 \times 10^{-3})AD$$

(2)

While the final equation in terms of coded factors is shown in Eq. (3):

$$y = 61.76 - 1.09a + 5.35b + 2.85c - 3.20d - 1.81ab - 1.24ac + 3.25ad$$

(3)

Therefore, for any A, B, C and D we can predict the percentage of liquefied OPT yield ($y$). The predicted $y$ is a function of A, B, C and D. For the equation in coded factors, the coefficients are in unitless.

3.4 Diagnostic checking of the fitted OPT liquefaction model

The predicted versus actual plot for liquefied OPT yield is presented in Fig. 5. The 45-degree line split the experimental values on the plot evenly, meaning that the correlation between these values is satisfied with $R^2$ value of 0.98. The small differences in comparison between the actual and predicted values of the liquefied OPT yield can be seen in Table 3 previously. It indicates that the model is reliable and the experiment was run carefully.

Besides, the normal probability versus internally studentized residuals were also plotted to check the model adequacy. The normal plot of residuals in Fig. 6 visually inspects whether the residuals follow a straight line. From here, it is concluded that the model had followed a normal distribution and the model is adequate. There was no abnormality observed in this study.

3.5 Response surface methodology plots

The response surface of the liquefied OPT yield that was generated will help in interpreting the effect of main factor and their interactions to the final yield. In the Fig. 7, the model for liquefied OPT yield in glycerol and ethylene glycol is presented. Meanwhile, the model for liquefied OPT yield in the mixture of both solvents with ratio 1:1 is being presented as a projection generated by the statistical software. Roughly, it can be seen that liquefaction of OPT in glycerol gave higher yield compared in ethylene glycol, while liquefaction of OPT in both solvent mixture is expected to yield somewhere in between the both. Highest yield obtained was 81.76% in liquefaction condition of 30 g OPT loading, 120 min liquefaction time, at 6% H$_2$SO$_4$ in glycerol.

In a study done by Jasiukaitytė et al. [33], they also found that lignin has less solubility in ethylene glycol with
OPT feedstock started to liquefy. At 120 min liquefaction time, 30 g OPT loading gave higher yield due to the higher ratio between solid and liquid. This can be related to the lignin and hemicelluloses started to dissolve \(^6\), thus made the mixture mixed well and permitted the solvent to attack more OPT particles.

In ethylene glycol, 60 g OPT loading gave higher yield compared to 30 g OPT loading at 10 min liquefaction time. As the liquefaction time increased, the amounts of yield obtained from 30 g OPT loading also increased and eventually surpassed that of 60 g. This happened due to thinner viscosity of ethylene glycol permitted the OPT feedstock to mixed well, even during the initial phase of the liquefaction process. In terms of catalyst, 6\% H\(_2\)SO\(_4\) gave higher yield compared to 2\%. One thing in common in all the liquefaction conditions was changes in OPT feedstock colour from light to dark brown can be seen as fast as 10 min liquefaction time (observation by naked eyes). This occurrence is in agreement with a study by Kurimoto et al. \(^36\).

In a study conducted by Yao \(^37\), he reported that rapid liquefaction in initial phase was due to degradation of lignin components, hemicelluloses and some reachable cellulose. The yield conversion ratio became slow later on because of hard-to-access cellulose. He concluded that the early liquefaction phase affected the conversion rate of the subsequent liquefaction stages.

### 4. Conclusion

Response surface methodology (RSM) through 2\(^{4-1}\) fractional factorial design could be used to determine the significant factor that affected the OPT liquefaction process. Factors like liquefaction time, types of solvents used and the percentage of H\(_2\)SO\(_4\) catalyst had significantly influenced the final liquefied OPT yield. In comparison, between ethylene glycol and glycerol as solvents, liquefaction of OPT in glycerol gave higher liquefied yield. The use of higher percentage of H\(_2\)SO\(_4\) catalyst and longer liquefaction time gave higher yield.

### Acknowledgment

We acknowledge the Ministry of Higher Education, Malaysia for the MyPhD Scholarship, MyBrain15.

### References

37) Yao, Y., Kyoto University, 1996