Process Simulation on Fast Pyrolysis of Palm Kernel Shell for Production of Fuel

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ABSTRACT

As the world's primary source of energy is depleting, an alternative particularly renewable energy is being explored. This work is a preliminary study on fast pyrolysis process of palm kernel shell to produce liquid fuel. The simulation uses pyrolysis data obtained from one of the previous works on fast pyrolysis of palm kernel shell. As there are no literature available on upgrading of bio oil from fast pyrolysis of palm kernel shell, the chemical reactions are synthesised based on upgrading of bio oil from different biomass. The upgraded oil is then analysed by comparing its distillate curve with that of the ASTM of gasoline. The distillation curves are shown to be quite similar as the components found in the oil almost resemble those in the gasoline. Thus, the bio oil from fast pyrolysis of palm kernel shell has almost similar components compared to the ASTM of gasoline.

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1. INTRODUCTION

The world energy demand is estimated to increase by 28% by 2040. Meanwhile, fossil fuel which is the primary source of energy is depleting (Andika and Valentina, 2016). Hence, renewable energy especially biomass is being explored as the alternative. In Malaysia, one of the most commonly found biomass are from oil palm industries. The waste mainly consists of empty fruit bunches (EFB), palm kernel shell (PKS), oil palm fronds (OPF) and oil palm trunks (OPT). About 83 million of oil palm biomass were produced back in 2012 and estimated to reach 100 million by 2020 (Awalludin et al., 2015).

One of the ways to utilize this waste is through pyrolysis. The three products of pyrolysis are gas, char and oil. Pyrolysis can be categorized into fast, slow and catalytic.
Slow pyrolysis produces mostly chars (Bridgwater, 2012) while catalytic pyrolysis has not much effect on the bio oil yield (Lim and Andrésen, 2011). Thus, fast pyrolysis is the most suitable method to produce bio oil (Bridgwater, 2012).

The oil produced however cannot be directly used as fuel due to high oxygen content and reactive nature (Bridgwater, 2012). There are a few upgrading methods to make the oil compatible to be used as fuel. These are hydrodeoxygenation (HDO), catalytic cracking, integrated hydropyrolysis and hydroconversion (IH2) and emulsification.

In catalytic cracking, the conceptual chemical reaction shows that oxygen is removed as water and carbon dioxide at high temperature (Bridgwater, 2012). The common type of catalyst used for this process is zeolite and modified metals (Zacher et al., 2014). Yet, the oxygen content in bio oil is still significantly high. This is reported due to the formation of coke on the catalyst surface (Elliott et al., 2009).

Apart from that, integrated hydropyrolysis and hydroconversion (IH2) is the recent technology used for bio oil upgrading. In this process, the biomass is pyrolysed at high temperature with pressurised hydrogen. The catalysts used for this process is obtained from the CRI Catalyst Company. The oil obtained has a low oxygen count (<0.5 wt%) (Marker et al., 2012).

Emulsification is the combination of diesel with bio oil to produce biodiesel. Emulsification requires the aid of surfactant as bio oil is immiscible in hydrocarbon (Xiu and Shahbazi, 2012). Through this, the bio oil can be directly used as fuel, however study reported that the corrosiveness of the biodiesel is too high causing this method to be economically unfeasible (Xiu and Shahbazi, 2012).

Hydrodeoxygenation (HDO) removes oxygen as water using pressurized hydrogen at high temperature (Bridgwater, 2012). This is the most common technology used for bio oil upgrading. The typical catalyst used are CoMo and NiMo. Several studies have also investigated using different types of metal catalyst. The overall conversion is satisfying as the oxygen content in bio oil is greatly reduced (Elliott et al., 2009; Luo et al., 2016).

This work is a preliminary study that models a complete fast pyrolysis process, including upgrading the oil through hydrodeoxygenation to produce fuel. The feed for this study is palm kernel shell (PKS) and the experimental data is obtained from Nurul Islam et al., 1999. This study also covers the synthesis of chemical reactions for the hydrodeoxygenation process and also the comparison on the distillate curve of the simulated process with the ASTM of gasoline.

2. MATERIALS AND METHODS

2.1. Methodology flowchart.

Figure 1 shows the flowchart for the overall methodology. Firstly, data on the bio oil components and the pyrolysis product yields are obtained (Nurul Islam et al., 1999). Then the hydrodeoxygenation (HDO) reactions for each of the bio oil components are synthesized.

Next, the entire process starting from the pretreatment of biomass until the separation process is simulated in Aspen Plus V8.8. Lastly, the distillate curve of the process obtained from the simulation is compared with the ASTM of gasoline.

2.2. Chemical reactions.

The two main reactions taking place in the process are pyrolysis and hydrodeoxygenation (HDO). The chemical reactions involved in both the reactions are further explained.
2.2.1. Pyrolysis

Pyrolysis is the thermal degradation of biomass at high temperature in the absence of oxygen. The three products of pyrolysis are oil, char and gas. In this work, the product yields tabulated in Table 1 are obtained from Nurul Islam et al. (1999).

2.1.2 Hydrodeoxygenation (HDO)

Hydrodeoxygenation (HDO) is an upgrading technique to convert the bio oil into transportation fuel. The operating conditions required for this process is at high temperature and high pressure (Elliott et al., 2009). Generally, hydrodeoxygenation process consist of hydrogenation and hydrocracking, however for simulation purpose, it is assumed to be a single reaction termed as hydrodeoxygenation (HDO).

In this work the hydrodeoxygenation (HDO) reactions are synthesised based on hydrodeoxygenation of different types of biomass. The bio oil components in Table 2 are used in this study.

Some of the components are not found in Aspen (indicated in Table 2). Thus, the compositions of these components are included with heavies.

For those components without literature on the hydrodeoxygenation process, it is determined using conceptual reaction reported by Bridgwater (2012). The heavies reported are replaced with dibenzofuran, C_{12}H_{8}O (dummy component) that has highest boiling point compared to the rest and a polycyclic nature.

Most importantly, from the synthesized reaction shown in Table 3, it is observed that the upgraded bio oil produced has a highest carbon number of 12. Thus, it is impossible to obtain diesel ranged hydrocarbons from this oil. At the same time, there are no literatures available to support this statement as the upgrading of pyrolysis oil from palm kernel shell is yet to be explored.

2.2. Process design

The operating conditions for the pyrolysis reactor and hydrodeoxygenation (HDO) reactor are given in Table 4. These conditions are used to simulate the process in Aspen Plus software. The process design methodology used in this paper is the same as in the literature (Bhullar and Putra, 2017; Putra, 2016a, 2016b).
Table 1. Pyrolysis product yields

| Product  | Yields (wt%) |
|-----------|--------------|
| Gas       | 16           |
| Char      | 26           |
| Bio oil   | 58           |

Table 2. Bio oil components (Nurul Islam et al., 1999)

| Bio oil components                          | Composition (wt%) |
|--------------------------------------------|-------------------|
| 2-Methyl propane                           | 0.52              |
| Acetic acid                                | 16.90             |
| 2,3-Hydroxy-2-propanone                    | 7.78              |
| 2,2-Methyl pentyl ether                    | 0.84              |
| 3-Butandial                                | 2.13              |
| 2-Allyl acetate-2-ene                      | 4.73              |
| 2-Furanaldehyde                            | 4.41              |
| 2-Butanone                                 | 0.84              |
| Methyl crotonate                           | 2.69              |
| Cyclopetanone                              | 1.34              |
| Phenol                                     | 28.3              |
| 1,3-Methyl cyclopentanedione                | 1.38              |
| 2-Methyl phenol                            | 0.79              |
| 2-Methoxy phenol                           | 4.82              |
| 4-Methyl 2-methoxy phenol                  | 2.02              |
| Ortho-hydroxy phenol                       | 2.16              |
| 4-Ethyl 2-methoxy phenol                   | 1.09              |
| 2,6-Dimethoxy phenol                       | 2.75              |
| 4-Propene 2-methoxy phenol                 | 1.36              |
| Heavies                                    | 15.76             |

Note: "Not found in Aspen Plus"
| Eq | Reaction | Conversion(X) | References |
|----|-----------|--------------|------------|
| (1) | C_2H_6O + 2H_2 \rightarrow C_2H_4O + H_2O | 0.55 | (Chen et al., 2011) |
| (2) | C_2H_2O + 4 H_2 \rightarrow 2CH_2 + 2H_2O | 0.17 | |
| (3) | C_2H_4O + 3H_2 \rightarrow C_2H_6 + 2 H_2O | 0.0092 | |
| (4) | C_6H_6O + H_2 \rightarrow C_8H_6O_2 | 0.055 | (Wang et al., 2018) |
| (5) | C_6H_6O + 2H_2 \rightarrow C_6H_6O + H_2O | 0.539 | |
| (6) | C_6H_6O + 5H_2 \rightarrow C_6H_12O + H_2O | 0.058 | |
| (7) | C_5H_4O + 4H_2 \rightarrow C_5H_10O + H_2O | 0.196 | |
| (8) | C_6H_6O + 4H_2 \rightarrow C_6H_10O_2 | 0.022 | |
| (9) | C_6H_6O + 2H_2 \rightarrow C_6H_10 + H_2O | 0.85 | (King et al., 2015) |
| (10) | C_6H_6O + H_2 \rightarrow C_6H_10O_2 | 0.80 | (Hu et al., 2015) |
| (11) | C_6H_6O + 2H_2 \rightarrow C_6H_10 + H_2O | 0.60 | (Liu et al., 2013) |
| (12) | C_6H_6O + H_2 \rightarrow C_6H_6O + H_2O | 0.145 | |
| (13) | C_6H_6O + H_2 \rightarrow C_6H_8 + H_2O | 0.254 | |
| (14) | C_6H_6O + 4H_2 \rightarrow C_6H_12 + H_2O | 0.80 | (Zhang et al., 2014) |
| (15) | C_6H_6O + 3H_2 \rightarrow C_6H_12O | 0.10 | |
| (16) | C_6H_6O + 4H_2 \rightarrow C_6H_14 + H_2O | 0.543 | (Whiffen and Smith, 2012) |
| (17) | C_6H_6O + H_2 \rightarrow C_6H_8 + H_2O | 0.457 | |
| (18) | C_7H_8O + H_2 \rightarrow C_6H_6O_2 CH_4 | 0.05 | (Mora-Vergara et al., 2018) |
| (19) | C_7H_8O + 2H_2 \rightarrow C_6H_6O + H_2O + CH_4 | 0.55 | |
| (20) | C_7H_8O + 3H_2 \rightarrow C_6H_6 + 2H_2O + CH_4 | 0.15 | |
| (21) | C_7H_8O + 2H_2 \rightarrow C_7H_8 + 2H_2O | 0.05 | |
| (22) | C_7H_8O + H_2 \rightarrow C_7H_8O_2 + H_2O | 0.15 | |
| (23) | C_7H_10O + 3H_2 \rightarrow C_7H_10 + 2H_2O | 0.025 | (Hsu and Lin, 2017) |
| (24) | C_7H_10O_2 + 2H_2 \rightarrow C_7H_10O + H_2O + CH_4 | 0.12 | |
| (25) | C_7H_10O_2 + 2H_2 \rightarrow C_7H_12O + H_2O + CH_4 | 0.151 | |
| (26) | C_7H_10O_2 + 6H_2 \rightarrow C_7H_14 + 2H_2O + CH_4 | 0.613 | |
| (27) | C_8H_6O + 6H_2 \rightarrow C_8H_6O + H_2O | 1.00 | (Gao et al., 2015) |
| (28) | C_8H_10O_2 + 6H_2 \rightarrow C_8H_10 + 2H_2O | 0.94 | (Chen, et al., 2015) |
| (29) | C_8H_10O_2 + 5H_2 \rightarrow C_8H_10O + CH_4 + H_2O | 0.01 | |
| (30) | C_8H_10O_3 + 2H_2 \rightarrow C_8H_10O_2 + CH_4 + H_2O | 0.626 | (Zhang et al., 2016) |
| (31) | C_8H_10O_3 + 7H_2 \rightarrow C_8H_12O + 2CH_4 + 2H_2O | 0.056 | |
### Table 3 (continued). Predicted chemical reactions for hydrodeoxygenation process

| Eq  | Reaction                                                                 | Conversion (X) | References           |
|-----|-------------------------------------------------------------------------|----------------|----------------------|
| (32)| \( \text{C}_{10}\text{H}_{12}\text{O}_{2} + 7\text{H}_{2} \rightarrow \text{C}_{9}\text{H}_{18} + 2\text{H}_{2}\text{O} + \text{CH}_{4} \) | 0.94           | (Chen et al., 2015)  |
| (33)| \( \text{C}_{10}\text{H}_{12}\text{O}_{2} + 6\text{H}_{2} \rightarrow \text{C}_{9}\text{H}_{18}\text{O} + \text{H}_{2}\text{O} + \text{CH}_{4} \) | 0.01           |                      |
| (34)| \( \text{C}_{12}\text{H}_{10}\text{O} + 6\text{H}_{2} \rightarrow \text{C}_{12}\text{H}_{20} \) | 0.05           | (Wang et al., 2013)  |
| (35)| \( \text{C}_{12}\text{H}_{10}\text{O} + 8\text{H}_{2} \rightarrow \text{C}_{12}\text{H}_{22} + \text{H}_{2}\text{O} \) | 0.90           |                      |
| (36)| \( \text{C}_{3}\text{H}_{6}\text{O}_{2} + 3\text{H}_{2} \rightarrow \text{C}_{3}\text{H}_{8} + 2\text{H}_{2}\text{O} \) | 0.779          | (Bridgwater, 2012)   |
| (37)| \( \text{C}_{6}\text{H}_{14} + \text{H}_{2} \rightarrow \text{C}_{6}\text{H}_{14} + \text{H}_{2}\text{O} \) | 0.779          |                      |
| (38)| \( \text{C}_{5}\text{H}_{8}\text{O}_{2} + 4\text{H}_{2} \rightarrow \text{C}_{5}\text{H}_{12} + 2\text{H}_{2}\text{O} \) | 0.779          |                      |

*Reactions based on conceptual equation*

### Table 4. Process condition for the simulated unit operations

| Process                                      | Temperature (°C) | Pressure (atm) | Ref                      |
|----------------------------------------------|------------------|----------------|--------------------------|
| Pyrolysis                                    | 500              | 1              | (Nurul Islam et al., 1999) |
| Condenser                                    | 0                | 1              |                          |
| Hydrodeoxygenation (HDO)                     | 400              | 103            | (Elliott et al., 2009)   |

### 3. RESULTS AND DISCUSSION

#### 3.1. Process description

The entire process is categorised into five parts as shown in the process flow diagram in Figures 2 and 3. Firstly, palm kernel shell (PKS) is fed into a grinder at 12500 kg/h. The feed is ground and sieved to 500 µm prior to pyrolysis. Lastly, the feed is dried. Drying is to reduce the moisture content of the feed to less than 10 wt% (Wright et al., 2010).

After pretreatment, the feed enters the pyrolysis reactor, where it is degraded at 500°C to produce gas, char and oil. Following pyrolysis, the products are sent to a cyclone where 90% of the solids are removed and condensed at 0°C to collect the bio oil produced. The bio oil is then sent to the decanter to separate the aqueous phase from the organic phase. Next, the bio oil is fed along with hydrogen into a hydrodeoxygenation (HDO) reactor. The hydrodeoxygenation reactor operates at 400°C and 103 atm.

The products, as stated in Table 4, are then sent for a series of separation to obtain the final output. The light gasses are firstly removed as vapor and distillate in DC 1. Major component, cyclohexane and the components with lesser boiling point are separated from the heavies in DC 2, followed by water removal in decanter, B5. The concentrated oil is then fed to DC 3 where methyl cyclohexane is purified up to its azeotropic composition. Lastly, in DC 4 the azeotropic components are separated and the final output with carbon number ranging from C5 to C7 is obtained.

The bottom of DC 2 is fed into DC 5 where the major component bicyclohexyl is separated at the bottom which is then further purified in DC 6. Distillate of DC 5 is fed to DC 7, where the ethyl cyclohexane and propyl cyclohexane are removed from the
heavies, consisting of unreacted raw materials. Water is removed as the distillate of DC 8 while the bottom is sent to DC 9 where ethyl cyclohexane and propyl cyclohexane are separated from the remaining impurities. All the liquid hydrocarbons are then mixed to form liquid fuels with carbon ranging from C₅ to C₁₂.

Figure 2. Process flow diagram for fast pyrolysis

3.2. Comparison on distillate curve

Distillate curve of the simulated process is constructed using the model analysis tool of Aspen Plus based on the hydrocarbons (C₅ to C₁₂) obtained.

The graphical comparison between ASTM of gasoline and the simulated process is shown in Figure 4. From the comparison, it is observed that at lower temperature (<100°C) simulated process have lesser lights compared to the ASTM of gasoline. On the other hand, beyond 100°C the simulated process has more heavies compared to the ASTM of gasoline.

No doubt, the upgraded oil can indeed be used as fuel. Since, the difference on the comparison between the ASTM of gasoline and upgraded oil has not much significance.
4. CONCLUSION

This is a preliminary study that simulate a complete fast pyrolysis of palm kernel shell process including the upgrading of the bio oil produced. For the upgrading methods, hydrodeoxygenation is used. The chemical reactions involved in the hydrodeoxygenation process for palm kernel shell is unavailable in the literature. Hence, it was synthesized based on hydrodeoxygenation of pyrolysis oil from different biomass as the final product would be the same (Elliott et al., 2009). From the synthesised chemical reactions, it was observed that the highest carbon number found in the pyrolysis oil from palm kernel shell is C_{12}. Thus, there are no diesel range hydrocarbon available from the pyrolysis oil. From the simulation, distillate curves that compares the simulated process with the ASTM of gasoline are obtained. The distillate curve shows that at lower temperatures (<100°C), the simulated results have lesser lights compared to the ASTM of gasoline and the otherwise is observed at higher temperature (>100°C).

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6. AUTHORS’ NOTE

We declare that there is no conflict of interest regarding the publication of this article. We have confirmed that the data and the paper are free of plagiarism.

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