# Sub- and Supercritical Hydrothermal Liquefaction of Oil Palm Biomass to Bio-oil

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*Abstract* - 3 types of Malaysian oil palm biomass with different lignocellulosic contents are liquefied using sub- and supercritical water to produce bio-oil. It is found that the optimum liquefaction conditions for the three types of biomass (EFB, PMF and PKS) using water are at supercritical conditions. PKS which consists of highest lignin content yields the maximum bio-oil of about 41.3 wt % at temperature of 450 ℃, followed by PMF and EFB obtaining bio-oil yields of about 39.6 wt % and 37.4 wt % at temperatures of 450 ℃ and 390 ℃, respectively.

*Index Terms* – oil palm biomass, hydrothermal liquefaction, bio-oil.

## I. INTRODUCTION

BIO-OIL is a liquid product derived from biomass which comprises of oxygenated compounds, various organic acids and other organic compounds such as aldehydes, ketones, phenols, alcohols and polyaromatic hydrocarbons (PAHs). Bio-oil is conventionally produced from fast pyrolysis process. Recently, sub-/supercritical liquefaction of biomass has gained attention as one of the promising methods to convert biomass to bio-oil. Subcritical liquefaction occurs at the temperature range of boiling point to critical point or near to critical point of the used solvent whereas supercritical liquefaction utilizes fluid formed at conditions above the critical temperature ($T_c$) and critical pressure ($P_c$) for that particular solvent [1]. In the supercritical regime, a fluid possesses unique properties in between liquid and gas. In this context, supercritical fluid possesses liquid-like densities but has high diffusivities and compressibilities similar to gas [2]. Therefore, supercritical fluid has enhanced solid solubility compared to liquid or gas solvent, making supercritical fluids ideal for separation and extraction of useful products.

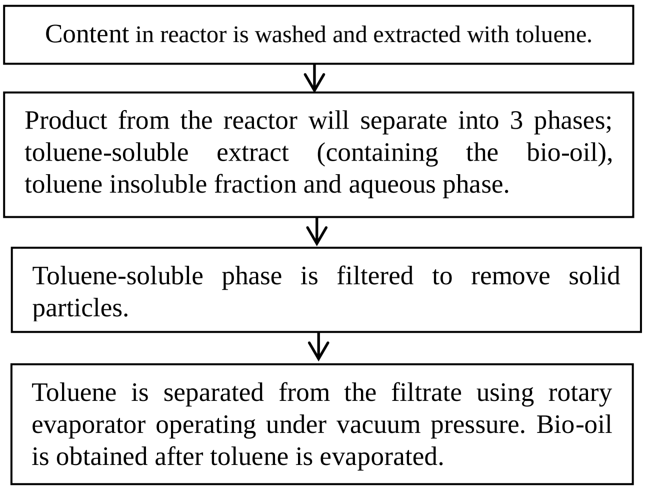
## II. EXPERIMENTAL

Palm biomass; empty fruit bunch (EFB), mesocarp fiber (PMF) and kernel shell (PKS) obtained were dried and grinded to a particle size of <710 µm with a FRITSCH Cutting Mill. These biomass were subjected to sub- and supercritical hydrothermal liquefaction conditions as shown in Table 1. The liquid (bio-oil) yields are determined for each experimental run at different temperatures and pressures. The liquefaction of biomass is carried out in 8.8ml Inconel batch reactor. Prior to the experiment, the densities of water at the experimental conditions (Table 1) were determined. Suitable amount of distilled water was loaded into the reactor such that it will produce the desired pressure at the reaction temperature.

Table 1: Conditions of Liquefaction

| Reaction conditions | Temperature ( ℃) | Pressure (MPa) |
|---|---|---|
| **Subcritical water** | 360 | 25 |
| | 360 | 30 |
| | 360 | 35 |
| **Supercritical water** | 390 | 25 |
| | 390 | 30 |
| | 390 | 35 |
| | 450 | 25 |
| | 450 | 30 |
| | 450 | 35 |

Biomass is loaded into the reactor at biomass to water ratio of 1:10. Once the biomass sample and distilled water were loaded into the reactor, the reactor was then inserted to the furnace set at the desired reaction temperature for a reaction time of 1 hour. After 1 hour, the reactor was removed from the furnace and quenched in water to atmospheric temperature. Then, the content in the reactor is washed and extracted thoroughly with toluene. Fig. 1 shows the flowchart of collecting the bio-oil from toluene extract.



Content in reactor is washed and extracted with toluene.

Product from the reactor will separate into 3 phases; toluene-soluble extract (containing the bio-oil), toluene insoluble fraction and aqueous phase.

Toluene-soluble phase is filtered to remove solid particles.

Toluene is separated from the filtrate using rotary evaporator operating under vacuum pressure. Bio-oil is obtained after toluene is evaporated.

Fig. 1: Flow chart for bio-oil collection

The bio-oil yield is then calculated using equation (1):

$$\text{Bio-oil yield (wt\%)} = \frac{\text{Weight of bio-oil obtained (g)}}{\text{Weight of biomass (g)}} \times 100 \qquad (1)$$

## III. RESULTS AND DISCUSSION

The yields of the bio-oil produced from the liquefaction of EFB, PMF and PKS are shown in Table 2.

Table 2: Bio-oil yields

| **Temperature (℃)** | **Pressure (MPa)** | **Bio-oil Yield from EFB (wt%)** | **Bio-oil Yield from PMF (wt%)** | **Bio-oil Yield from PKS (wt%)** |
|---|---|---|---|---|
| 360 | 25 | 25.31±0.44 | 22.71±0.83 | 26.55±1.29 |
| 360 | 30 | 26.02±0.44 | 23.22±0.54 | 27.54±0.70 |
| 360 | 35 | 22.76±0.28 | 21.75±0.01 | 23.44±1.24 |
| 390 | 25 | **37.39±0.67** | 34.32±1.87 | 38.53±1.46 |
| 390 | 30 | 28.17±0.35 | 27.57±1.03 | 31.16±0.81 |
| 390 | 35 | 30.16±0.98 | 24.07±1.04 | 29.35±0.71 |
| 450 | 25 | 36.66±1.94 | 34.44±1.07 | 34.62±0.49 |
| 450 | 30 | 36.03±0.13 | **39.67±1.52** | **41.31±1.65** |
| 450 | 35 | 35.62±0.54 | 35.99±1.94 | 37.39±0.83 |

The optimum hydrothermal liquefaction for bio-oil production is at supercritical condition for EFB, PMF and PKS. Supercritical fluid possesses high densities and high diffusivities and compressibilities. Supercritical water is able to dissolve and extract materials which are normally water insoluble. Besides, supercritical water promotes higher reactivity and better separation and extraction. Therefore, supercritical fluid has enhanced solid solubility compared to liquid or gas solvent, making supercritical fluids ideal for separation and extraction of useful products. In this study, it is found that the optimum liquefaction condition for EFB is at a lower supercritical temperature of 390 ℃ and higher supercritical temperature of 450 ℃ for PMF and PKS (Table 2). This is due to the difference in the lignocellulosic contents from the structural analysis of the biomass (Table 3).

Table 3: Lignocellulosic content of oil palm biomass

| **Biomass** | **Cellulose (%)** | **Hemicellulose (%)** | **Lignin (%)** |
|---|---|---|---|
| EFB | 26.6 | 26.9 | 18.6 |
| PMF | 23.1 | 22.2 | 30.6 |
| PKS | 24.5 | 22.9 | 33.5 |

Hemicellulose is a hetero-polymer which composed of various side-groups. Hence, it has a less uniform structure and lower degree of crystallinity [3] and can be easily decomposed at lower temperatures between 210-330 ℃. Cellulose has a higher degree of crystallinity as it consists of long polymers of glucose units without branches [4]. Thus, higher temperature between 300-375 ℃ is needed to break the cellulose structure from the matrix structure of biomass. Lignin is a highly crossed-linked polyphenolic aromatic polymer having no ordered repeating units. As such, lignin has the highest thermal stability compared hemicellulose and cellulose and can be decomposed at a wide range of temperatures between 150-1000 ℃ [4]. EFB has lower lignin content compared to PMF and PKS although the former has slightly higher cellulose and hemicellulose contents. Therefore, the optimum reaction temperature for EFB is lower compared to that of PMF and PKS, as higher temperature (450 ℃) is able to decompose lignin and form bio-oil. In this study, the yields of bio-oil produced using supercritical water are higher compared to a study using oil palm fruit press fiber, which give optimum yields of 30.0, 30.4 and 32.4 wt% using supercritical methanol, ethanol and acetone respectively [5].

However, increasing pressure has different impacts on the bio-oil yield. Higher pressure increases solvent density and solubility of the target biomass components, thus allowing the solvent to penetrate more efficiently into molecules of biomass components, hence enhancing decomposition and extraction. On the other hand, increased pressure causes cage effect for the C-C bonds in biomass. This effect inhibits C-C bonds cleavage and fragmentation [6]. Hence, determination of optimum pressure level suitable for sub- and supercritical liquefaction of biomass to obtain high yields of bio-oil should be given further consideration.

## IV. CONCLUSION

Optimum temperature for hydrothermal liquefaction of biomass is specific to the types of biomass. Higher optimum reaction temperature of PMF and PKS is due to its higher lignin content, which decomposes at higher temperature compared to EFB. Pressure imparts different influences on the bio-oil yields and further studies need to be done to address the effect of pressure on the bio-oil yields.

## V. ACKNOWLEDGEMENT

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