

Conversion of Oil Palm Biomass to Bio-oil Under Sub- and Supercritical Conditions

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ABSTRACT

In this study, the production of bio-oil from oil palm biomass (empty fruit bunch and mesocarp fiber) under sub- and supercritical liquefaction are investigated under various sub-/supercritical temperatures of water (360, 390 or 450 °C) and pressures (25, 30 or 35 MPa). It is found that the optimum liquefaction conditions for the two types of biomass using water are at supercritical conditions, with EFB and PMF yielding 37.4 wt% and 39.7 wt% at temperatures of 390 °C and 450 °C respectively.

1. 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 subcritical condition and 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.

2. EXPERIMENTAL

Empty fruit bunch (EFB) and mesocarp fiber (PMF) of palm biomass 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 liquefaction reaction 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 8.8 ml 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 (°C)	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.

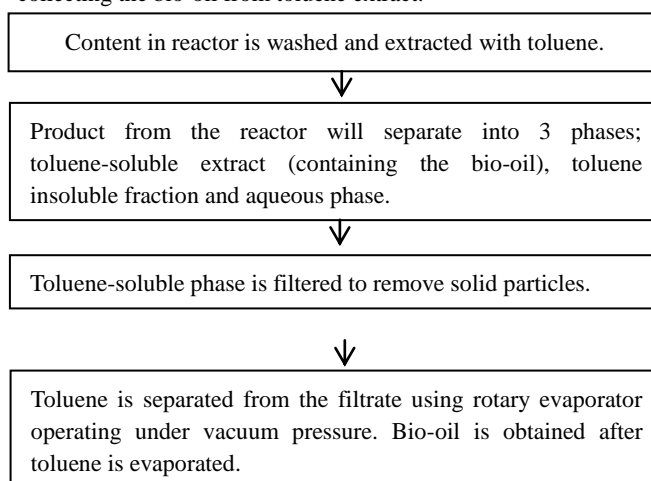


Fig 1: Flow chart for bio-oil collection

The bio-oil yield is then calculated using equation:

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

3. RESULTS AND DISCUSSION

The yield of the bio-oil produced from the liquefaction of EFB and PMF is shown in Table 2.

Table 2: Bio-oil yields

Temperature (°C)	Pressure (MPa)	Bio-oil Yield from EFB (wt%)	Bio-oil Yield from PMF (wt%)
360	25	25.31±0.44	22.71±0.83
360	30	26.02±0.44	23.22±0.54
360	35	22.76±0.28	21.75±0.01
390	25	37.39±0.67	34.32±1.87
390	30	28.17±0.35	27.57±1.03
390	35	30.16±0.98	24.07±1.04
450	25	36.66±1.94	34.44±1.07
450	30	36.03±0.13	39.67±1.52
450	35	35.62±0.54	35.99±1.94

The optimum condition for bio-oil production is at supercritical condition for both EFB and PMF. In the supercritical regime, supercritical fluid possesses liquid-like densities but has high diffusivities and compressibilities similar to gas. 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 °C and higher supercritical temperature of 450 °C for PMF (Table 2). This is due to the difference in the lignocellulosic content from the structural analysis of both 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

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 °C. 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 °C is needed to break the cellulose structure from the matrix structure of biomass. Lignin is a highly cross-linked polyphenolic aromatic polymer having no ordered repeating units. As such, lignin has the highest thermal stability compared hemicellulose and cellulose [4]. As such, lignin can be decomposed at a wide range of temperatures between 150-1000 °C. EFB has lower lignin content compared to PMF although the former has slightly higher cellulose and

hemicellulose contents. Therefore, the optimum reaction temperature for EFB is lower compared to that of PMF, as higher temperature (450 °C) 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.

4. CONCLUSION

The optimum hydrothermal liquefaction condition of EFB and PMF is at supercritical temperatures of 390 °C and 450 °C respectively. Higher optimum reaction temperature of PMF is due to its higher lignin content, which decomposes at higher temperature. 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.

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