Thermal pyrolysis of empty fruit bunch (EFB) in a vertical fixed-bed reactor

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Abstract. In the production of crude palm oil, huge quantities of solid biomass waste is generated such as empty fruit bunch (EFB), palm fronds and palm–pressed fibre (PPF). This inevitably resulted in the environmental pollution due to its natural conversion to methane. In this study, thermal pyrolysis of EFB was conducted using a fixed bed reactor. The factors such as nitrogen gas flowrate and holding time that affect the distribution of pyrolysis product yields were being investigated by evaluating the percentage product yields. It was determined that at nitrogen gas flowrate of 300 cm³/min and 30 mins holding time, the maximum bio-oil yield of 46.20% was attained with gas and char yield of 21.79% and 32.01% respectively. The existence of functional groups in bio-oil was analyzed by Fourier Transform Infra-Red (FTIR) spectroscopy. It was identified that the bio-oil has several functional groups such as hydroxyl (OH), ketone/aldehyde (C=O) and ester (O-C=O) groups. The dynamic viscosity of bio-oil was analyzed by Brookfield viscometer. It showed that the viscosity of bio-oil decreased with increasing temperature from 25-50 °C.

1. Introduction
In the palm oil mill extraction process, approximately 20% crude palm oil was produced from the total biomass and the balance 80% accounted for waste which was usually discarded off. Usually, one tonne of fresh fruit bunch produced almost 0.31–0.35 tonnes of palm oil effluent (POME) with 0.20 – 0.30 tonnes of empty fruit bunches (EFB) [1]. Obviously, EFB is one of the main solid waste produced during palm oil extraction process. Thermochemical processing such as torrefaction and pyrolysis have been reported for the conversion of biomass into torrefied biomass/bio-char, liquid bio-oil and gases products [2, 3]. Combination of consequential pretreatment such as torrefaction and demineralization has improved the energetic properties of EFB [4]. Biomass pyrolysis is defined as thermochemical process over the biomass at increasing temperature in the oxygen-free environment [5]. Several research works were reported in the literature emphasizing the importance of pyrolysis process parameters towards improving the liquid bo-oil yields [6, 7, 8]. The optimization of process parameters using Response Surface Methodology (RSM) towards maximizing bio-oil yield has also been reported [9,10]. Basically, these reported studies focused on the manipulation of process parameters towards achieving the highest bio-oil yield. One of the important physical property of fresh bio-oil is viscosity. Apart from other physico-chemical properties of fresh bio-oil, viscosity can be used to determine the prominance of bio-oil as bio-lubricant.

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The viscosity of EFB bio-oil from non-catalytic and catalytic pyrolysis with CaO, MgO at 35 °C were reported and generally the viscosity decreased approximately from 1.5 to 1.0 cSt [11]. The dynamic viscosities of several ethylene glycol di-esters (EGDEs) which were produced from the transesterification of vegetable oil such as sunflower, soybean, jatropha and waste oil with a di-alcohol were reported that indicated the importance of dynamic viscosity of oil in order for it to function as biolubricant [12]. In relation to that, it is identified that the study on process parameters towards maximizing EFB bio-oil yield together with the dynamic viscosity of fresh bio-oil at several range of temperature is scarce. Therefore, this paper reports the effect of two process parameters namely nitrogen gas flowrates and holding time towards maximizing EFB bio-oil yield with the dynamic viscosity of fresh bio-oil at a certain range of temperature.

2. Materials and methods

2.1. Biomass pretreatment
EFB was obtained from palm oil mill North Star Palm Oil Mills which is located in Kuala Ketil, Kedah. The biomass was rinsed with tap water to remove impurities and chopped manually. It was dried in the oven for 24 hours at 80 °C. It was shredded using shredding machine and sieved using the Retsch sieve shaker. The EFB with particle size of 250-500 μm was selected for the pyrolysis process [13].

2.2. The ultimate and proximate analyses
The elemental and proximate analyses were conducted on the EFB. The elemental analysis was carried out using Perkin Elmer elemental analyzer series II CHNS/O 2400. The proximate analysis was conducted on the EFB sample with particle size in the range of 125-250 μm in accordance with the ASTM. The moisture content was determined following the ASTM E871-82. The volatile matter and ash contents were determined according to ASTM E872-82 and ASTM D1102-84 respectively. The fixed carbon content was estimated by difference.

2.3. The pyrolysis experiment
Approximately 10.00 g of EFB was packed in the reactor tube which was placed in the fixed-bed reactor for pyrolysis. In the first series of experiments, the effect of nitrogen gas flowrates on the distribution of pyrolysis products was studied. The nitrogen gas flowrates were varied at 100, 200, 300, 400 and 500 cm³/min. The pyrolysis temperature was measured by the temperature set in the programmable controller. In each experiment, the pyrolysis was ignited when the pyrolysis temperature was set to pyrolysis temperature of 500 °C, at a ramp rate of 20 °C/min and kept isothermal for 30 mins. The reactor was purged with nitrogen gas for 30 mins at 2 bars at a flowrate of 100 cm³/min. The temperature of the furnace was increased accordingly upon ignition while the temperature was measured by a thermocouple located close to the reactor tube. After completion of holding time, the reactor tube was cooled under the nitrogen stream. The flasks were weighed before and after each experiments and the bio-oil yield was estimated by difference. The bio-char was removed from the reactor tube and its mass was recorded. The weight percentages of bio-char, bio-oil were determined by weighing. The percentage of gas was calculated by difference. After removal of char and glass wool from the reactor tube, acetone was pumped into the reactor tube and condenser line until clear solution was obtained to ensure that it was fully cleaned and ready for next experiment. The second series of experiment were conducted to determine the effect of holding time. The final pyrolysis temperature was 500 °C at a fixed heating rate of 20 °C/min. However, the final pyrolysis temperature was kept isothermal at different holding time of 10, 20, 30, 40 and 50 mins. The experiments were conducted in triplicates to provide standard deviation for the data less than ±5.0 wt% [2, 14, 15]. The yield of products was determined by the Eqns 1, 2 and 3:
2. Bio-oil properties

The bio-oil obtained at nitrogen gas flowrates of 300 cm$^3$/min and holding time of 30 mins was collected and characterized. The dynamic viscosity of the fresh bio-oil at temperature from 25-50 °C was obtained using Brookfield Viscometer LVDV-I Prime with accessory UL Adapter (Open Tube). The functional groups exist in the bio-oil was identified using Perkin Elmer Fourier Transform Infra-Red (FTIR) spectroscopy. The bio-oil was mounted onto ATR accessory and 4 scans were carried out at wavenumber range from 4000-650 cm$^{-1}$.

3. Results and Discussion

3.1 Biomass properties

The ultimate and proximate analyses of EFB are as shown in Table 1. EFB has high carbon and volatile matter contents with low moisture content thus making it a prominent source of energy.

| Table 1: The ultimate and proximate analysis of EFB |
|-----------------------------------------------------|
| The ultimate analysis on EFB | C (%) | H (%) | N (%) | S (%) | O (%) (by difference) |
|-------------------------------|-------|-------|-------|-------|-----------------------|
| EFB                           | 47.08 | 8.01  | 1.02  | 1.32  | 42.57                 |

| The proximate analysis of EFB | Moisture content (%) | Volatile matter (%) | Fixed carbon (%) | Ash Content (%) |
|-------------------------------|----------------------|---------------------|------------------|----------------|
| EFB                           | 7.39                 | 76.25               | 11.18            | 5.18           |

3.2 The effect of nitrogen gas flowrates on the products yield

Figure 1 shows the pyrolysis products yield from slow pyrolysis of EFB at various nitrogen gas flowrates such as 100, 200, 300, 400 and 500 °C/min at constant heating rate of 20 °C/min towards final pyrolysis temperature of 500 °C and kept isothermal for 30 mins.

![Figure 1. The distribution of pyrolysis products against the nitrogen gas flowrates.](image-url)
The bio-oil yield showed an increasing trend from 41.07 % at 100 cm³/min and reached a maximum of 46.20 % when the nitrogen gas flowrates was increased from 100 to 300 cm³/min. When the nitrogen gas flowrates was increased to 400 cm³/min, the bio-oil yield was reduced and further increasing of the flowrates to 500 cm³/min did not change the bio-oil yield. It was identified that at nitrogen gas flowrates of 300 cm³/min, the highest bio-oil yield of 46.20 % was attained. This is because the nitrogen sweeping gas reduced the residence time of the hot vapours produced during biomass pyrolysis, thus, minimizing secondary reactions [16]. The sweeping gas minimized the secondary reactions by quickly removed the hot vapours from the hot reaction zone into the cooling apparatus [17]. The bio-oil could be maximized by avoiding the phenomena of secondary cracking reactions or by maximizing the primary pyrolysis reactions [16]. The bio-oil yield showed slight reduction at higher nitrogen gas flowrates could be due to insufficient cooling of the condensation apparatus [17].

The bio-char yield was consistent in the range of 21.87-22.62 % from nitrogen gas flowrates of 100-500 cm³/min. This indicated that the sweeping nitrogen gas flowrates seemed to have no significant role in the bio-char and gas yields. This observation was quite similar to [18, 16, 17]. The nitrogen gas flowrate has no significant influence in the bio-char yield because the secondary reactions may have been minimized or inhibited with the application of high nitrogen gas flowrates. If the nitrogen gas flowrates posed significant influence on the bio-char yield, it would have decreased over increasing nitrogen gas flowrates due to secondary cracking or further decomposition of bio-char fraction. Usually, the trend was seen particularly with the application of final pyrolysis temperature [20]. This, however, was not evident from the current study. Therefore, it was suggested that the nitrogen flowrates had successfully inhibited secondary cracking reactions over the hot bio-char fractions at all its corresponding flowrates. The trend shown by the bio-oil yield also agreed with this finding.

In addition, the gas yield was reasonable at 36.31 % when the nitrogen gas flowrate at 100 cm³/min. This however reduced to 32.01 % at nitrogen gas flowrates of 300 cm³/min and increased to 36.05 % when the maximum nitrogen flowrate of 500 cm³/min was applied to the reactor because the condensation apparatus unable to quench the huge amount of condensable gases efficiently [17].

### 3.3 The effect of holding time on the products yield

The pyrolysis products yield from slow pyrolysis of EFB at various holding time of 10, 20, 30, 40 and 50 mins at constant heating rate of 20 °C/min towards final pyrolysis temperature of 500 °C is as shown in Figure 2.

![Figure 2. The distribution of EFB products at various holding time.](image)
The bio-oil yield increased from 39.37% to 46.20% when the holding time was increased from 10 mins to 30 mins. This was in good agreement with [21]. Further increasing the holding time seemed to reduce the bio-oil yield due to secondary reactions of pyrolysis vapours [21]. This could be due to the fact that increasing the holding time favoured the active pyrolysis stage. Secondly, increasing the holding time also favoured the primary pyrolysis reactions and inhibited the secondary reactions.

The bio-char yield was quite consistent at approximately 21.70% - 22.67% at various holding time. The holding time seemed to have no significant influence on the bio-char yield. Non-reduction of bio-char over various holding time also suggested that the primary reactions during pyrolysis process were the prevailing reactions compared to the secondary reactions. Secondary reactions seemed to be successfully inhibited when the holding time was increased from 20-50 mins.

A good indication on the occurrence of the secondary reaction was the reduction of bio-char and bio-oil yields as well as increasing gas yield [20]. Both of these seemed to occur because the hot-biochar fraction reacted with hot vapour newly formed as well as it underwent further decomposition due to high temperature effect. However, both of these indications were not observed here. Therefore, it would strongly suggested that secondary reactions had been successfully inhibited when the holding time was increased from 20 to 50 mins.

The gas yield was at its highest of 37.97% when the holding time was set at 10 mins but decreased to 32.02% when the holding time was increased to 20 mins. Further increasing the holding time did not seemed to change the gas yield significantly. It was consistent at about 32.01-31.59% at holding time from 30-50 mins.

The FTIR spectrum of bio-oil is as shown in Figure 3. The huge and wide peak at approximately 3394 cm\(^{-1}\) corresponded to the existence of hydroxyl group (O-H) from organic acids or hydroxyl group [22-25]. The small peak at approximately 2927 cm\(^{-1}\) indicated the presence of hydrcarbon (C-H) group [22-25]. The carbonyl group was recorded at wavenumber of 1711 cm\(^{-1}\) as well as 1270 cm\(^{-1}\) which indicated the presence of C=O from ester, aldehyde or ketone groups [22-25]. A single and small peak at approximately 1380 cm\(^{-1}\) could be attributed to the presence of C-H alkanes [22].

![Figure 3. The FTIR spectrum of bio-oil](image)

The dynamic viscosity of the fresh bio-oil was plotted in Figure 4. In general, the viscosity of the fresh bio-oil showed a decreasing pattern when the temperature was increased from 25 to 50 °C. The maximum viscosity of 3.70 mPas was recorded at temperature of 25 °C. When the temperature was increased, the viscosity started to decrease. However, the viscos city seemed to increase slightly at 40 °C. This could be due to certain reactions occurring within the bio-oil that was initiated by the temperature. However, further increasing of the temperature seemed to decrease the bio-oil viscosity. This is in good agreement with reported study by Hafis et al. [26].
4. Conclusion

The pyrolysis of empty fruit bunch (EFB) was conducted using a fixed bed reactor. The two process parameters such as nitrogen gas flowrates and holding time that affected the distribution of pyrolysis product yields were being investigated by evaluating the percentage product yields. It was identified that at the optimum nitrogen gas flowrates of 300 cm³/min and 30 minutes holding time, a maximum bio-oil yield of 46.20% was achieved with gas and char yield of 21.79% and 32.01% respectively. The FTIR analysis on bio-oil showed that it contained O-H group from carboxylic acids or hydroxyl group, hydrocarbon C-H group as well as carbonyl (C=O) group originating either from ester, carboxylic, aldehyde or ketone groups. The dynamic viscosity of bio-oil decreased over increasing temperature from 25 - 50 °C.

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