Gasification of pre-treated palm based empty fruit bunches: effect of alkali metal content

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Abstract. This study shows that pre-treatment of empty fruit bunches (EFB) has a positive impact on the energy content of syngas from the gasification process. In Malaysia, there is an estimated 25 million tonnes of EFB which can be used for power generation or for producing value added products through gasification. Gasification is a thermochemical process where the oxidant (air) is lower than the stoichiometric requirement, thus producing volatile syngas such as carbon monoxide, methane, hydrogen that contribute to the energy content. However, EFB has relatively higher ash and alkali metal content compared to other types of biomass, such as wood. Alkali metal contents such as potassium and sodium (K and Na) have been reported to reduce the initiation temperature for the formation of slag and clinker, and can cause operational issues for gasification systems, though other results show that alkali metals increase the gasification reactivity. Pre-treatment of the EFB may be required for reducing alkali metal related operational issues, and increase the performance of gasification in terms of the energy content of the syngas. Thus, this study investigates the effect of pre-treatment on the properties of the EFB, with a focus on the alkali metal content. The correlation between the pre-treatment (and the alkali metal content) on the yield and composition of the syngas from the gasification process is investigated.

1. Introduction
Malaysia is the second largest producer of palm oil in the world and the resulting oil palm waste can create a waste management issue [1]. The oil palm waste could be transformed into value added products by the thermochemical processes such as combustion, gasification and liquefaction. About 25% of the wastes such as empty fruit bunches (EFB), palm kernel shell (PKS) and mesocarp fibre (MF) are used for combustion to generate electricity [1]. The annual amount of EFB is approximately 25 million tonnes, which is higher compared to PKS, trunks, and fronds [2]. However, the energy content of EFB is lower compared to PKS (18.8 MJ/kg [2]).

Despite the lower energy content of EFB, it is a potential feedstock for power generation, and furthermore could be converted into other value added products through gasification. Gasification is a thermochemical process where the oxidant (usually air) is lower than the stoichiometric requirement, thus producing volatile syngas such as carbon monoxide, methane, hydrogen that contribute to the energy content. The high volatile matter content in EFB (between 60 to 80%) makes it highly reactive [3], potentially providing hydrocarbons (such as carbon monoxide and hydrogen) that could synthesized further to produce chemicals (e.g., methanol). In addition, EFB contains a higher amount of cellulose
(56.4%) compared to PKS (33.4) [4] and other types of biomass such as coconut shell (17.9%) [5] and sugarcane bagasse (25-45%) [6]. A higher cellulose content makes EFB a suitable feedstock for conversion into biofuels [7].

However, EFB has high ash content and alkali metal [8]. Alkali metal contents such as potassium and sodium (K and Na) have been reported to reduce the initiation temperature for the formation of slag and clinker, and can cause operational issues for gasification systems, though other results show that alkali metals increase the gasification reactivity [6]. Thus, this study investigates the effect of pre-treatment on the properties of the EFB, with a focus on the alkali metal content. The correlation between the pre-treatment (and the alkali metal content) on the yield and composition of the syngas from the gasification process is investigated as well.

2. Methodology

2.1. Characterization of EFB samples

EFB samples were characterized using Thermo-MASS TG-DTA equipment to determine the thermal analysis study. Fuel characterization can be determined from this analysis such as pyrolysis and combustion behaviour [9]. Heating rate 10°C was used and 5.6 mg of EFB samples were prepared inside the crucible with the raised temperature from 26.5°C to 899°C. TGA was carried out in an ambient environment for all three types of EFB. From the analysis, the value of moisture content, volatile matter, fixed carbon and ash were determined from each EFB sample. The value for each part determined from the graph obtained from the TGA analysis. CHNS analysis were carried out using CHNS analyser with the model type Elementar. The value of carbon, nitrogen, hydrogen and sulphur can be examined from this analysis. The method used for combustion separation is by Temperature Programmed Desorption (TPD) which is the chromatographic technique for the determination of non-metal elements. The heating value of EFB samples also measured using bomb calorimeter. The calorific value is the amount of heat energy released from the combustion of feedstock. The sample was placed in a high pressure oxygen filled combustion vessel and the value of energy was determined from the samples of CR, CS and G. The heating value was determined using ASTM D4809-00 by equipment Leco AC-350 bomb calorimeter [10].

2.2. Gasification of EFB samples

Pulverized EFB samples of 1 to 5 mm (Figure 4) are divided are used for experiments, denoted as raw EFB, EFB A and B samples. The pre-treatment process for EFB A and B are performed by leaching the EFB with water at an EFB-to-water ratio (EW) of 1:10 and 1:7.5 respectively. The EFB samples are fed into a downdraft gasifier (Figure 5) to produce syngas. Raw EFB was gasified at temperatures 600°C, 700°C, 800°C and 900°C and at air flow rates of 1.0 to 5.0 L/min. Based on the operational conditions during the gasification of the raw EFB samples and the syngas composition (which determines the energy content), a set of optimum process parameters for the temperature and air flow rates are selected for the gasification of EFB A and B.

The higher heating value (HHV) of the syngas depends on the energy content and volumetric fraction of CO, H₂ and CH₄ (Xₜ₉, Yₕ₂ and Zₜ₄):

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\text{HHV}_{\text{syngas}} = \text{HHV}_{\text{CO}} \times X_{\text{CO}} + \text{HHV}_{\text{H₂}} \times Y_{\text{H₂}} + \text{HHV}_{\text{CH₄}} \times Z_{\text{CH₄}}
\] (1)

The HHV for CO, H₂ and CH₄ are 12.63MJ/m³, 12.75MJ/m³, and 39.72 MJ/m³ respectively [1].
Figure 1  EFB samples (a) EFB treated A (b) EFB treated B (c) Raw EFB

Figure 2  (a) Schematic diagram of downdraft gasifier (b) Downdraft gasifier
3. Results and Discussion

3.1. Characterization of EFB samples
Table 1 depicts the proximate analysis of the EFB samples. Raw EFB has the highest moisture content at 13.14%, while EFB A has the lowest moisture content. The difference in the moisture content could be caused by changes in the structure of the EFB after pre-treatment, since the lignin, hemicellulose and cellulose contents may have change the EFB’s hygroscopic nature Future work is required to investigate the pre-treatment’s effect on the EFB’s ability to absorb moisture. Table 1 also shows that a higher EW ratio for EFB A reduces the ash content via leaching with water compared to raw EFB and EFB B, reducing it to 4.07%. The reduction of the ash content increases the volatile matter and fixed carbon contents, with EFB A having the highest corresponding values at 70.65% and 16.37% respectively. The results are similar to those in literature where leaching of EFB via water reduced the ash content by 24.9%-70.3% [12]. In this study, the ash content was reduced by 57% with a EW ratio of 1:10.

Table 1 TGA results of EFB samples

| EFB samples | Moisture Content (w%) | Volatile Matter (w%) | Fixed Carbon (w%) | Ash Content (w%) |
|-------------|-----------------------|----------------------|-------------------|-----------------|
| Raw         | 13.14                 | 64.36                | 15.35             | 7.15            |
| EFB B (EW1:7.5) | 10.64            | 68.09                | 15.95             | 5.32            |
| EFB A (EW1:10)   | 8.92                 | 70.65                | 16.37             | 4.07            |

Table 2 shows that EFB A has the highest carbon and hydrogen content (43.64% and 6.16% respectively). A higher content of hydrogen is associated with a strong water gas reaction. Lower content of nitrogen (1.21%) and sulphur (0.20%) shows that the fuel is eco-friendly since less NOx and SOx are emitted.

Table 2 CHNS analysis from EFB samples

| EFB samples | Carbon (w%) | Hydrogen (w%) | Nitrogen (w%) | Sulphur (w%) | Oxygen (w%) |
|-------------|-------------|---------------|---------------|--------------|-------------|
| Raw         | 38.47       | 5.71          | 1.32          | 0.44         | 54.05       |
| EFB B (EW1:7.5) | 41.37       | 5.97          | 1.40          | 0.19         | 51.07       |
| EFB A (EW1:10)   | 43.64       | 6.16          | 1.21          | 0.20         | 48.79       |

Calorific value of EFB A samples was 17.1 MJ/kg and followed by EFB B (16.9 MJ/kg) and raw EFB samples (16.45 MJ/kg) as presented in Figure 4. EFB A has the highest calorific value since the ash content is the lowest (Table 1) and the carbon content is the highest (Table 2). A higher carbon content indicates higher carbon–carbon bonds, which contributes to the energy content. Conversely, the oxygen content forms carbon-oxygen bonds which reduces the energy content.
3.2. Gasification of pre-treated EFB samples

Figure 4 shows the syngas composition from the gasification of raw EFB samples at different temperatures (700-900°C). At 900°C, the composition of CO and H₂ are 13.34% and 8.84% respectively; at 700°C the CO and H₂ are 2.00% and 4.47% respectively. The increase of CO and H₂ with increasing temperature is due to the water gas, Boudouard reactions. Also, higher temperatures increases the rate of char gasification and cracking of hydrocarbon containing tar compounds into CO and H₂ [2]. The higher CO and H₂ increases the HHV of the syngas, with a value of 3.24 MJ/Nm³ at 900°C (Figure 5). CO₂ is the highest at 800°C, indicating that the gasification reaction has shifted from gasification to combustion. The lower amount of CH₄ (0.74%) at 800°C indicates a consumption of CH₄ due to exothermic reactions [3].
At 900°C, the gasification process was unstable, causing the feeding of the raw EFB to be inconsistent. Therefore, a temperature of 800°C and AFR of 2.5 l/min are used for the gasification of EFB A and B. Figure 6 shows that syngas from EFB B has CO, CH$_4$, and H$_2$ of 11.12, 1.60 and 8.81%, and syngas from EFB A has a CO, CH$_4$ and H$_2$ composition of 11.00, 2.56 and 9.59%. Figure 7 shows the HHV for EFB A has the highest HHV compared to the other two of biomass samples with a value of 3.63 MJ/Nm$^3$. HHV depends on the value of CO, H$_2$ and CH$_4$. As the value of these three composition increases, HHV also increases.

The difference in the syngas composition is due to the varying pre-treatment methods, where different amounts of water (i.e. the EW ratio) is used for leaching the EFB. Table 1 and 2 showed that at an EW ratio of 1:10, EFB A has the lowest ash content, and the highest carbon content. Gasification of fuel with high carbon and low ash contents allows the production of syngas with higher HHV, thus show the advantage of pre-treating the fuel.

In addition, pre-treatment also reduces slag and clinker inducing alkali metal contents, resulting in less operational issues during gasification. Table 3 shows that the alkali metal content (K+Na) is reduced to 0.54% with an EW ratio of 1:10, compared to the raw EFB which has a (K+Na) content of 1.65%. Chlorine, silica and calcium are reduced with an increase in EW ratio as well. No significant effect was observed for iron, magnesium and aluminium with a change in the EW ratio. The synergistic effects of alkali metal content on the syngas composition from gasification is not significant as reported [4]. The ash and carbon contents of the biomass may have a more pronounced effect on the gasification process [5].

The HHV$_{syngas}$ in this study is below the reported average values of 6 MJ/Nm$^3$ [6]. Using air as the gasifying agent, a lower calorific value is produced. If the syngas was used in an internal combustion engine to generate power, the low HHV$_{syngas}$ may affect the engine performance. A further strategy needs to be investigated to enhance the gasifier performance, increasing the HHV$_{syngas}$ for power generation.
Table 3: Alkali metal and other inorganic element contents of EFB samples

| EFB samples       | K+Na (w%) | Cl (w%) | Si (w%) | Ca (w%) | Fe (w%) | Mg (w%) | Al (w%) |
|-------------------|-----------|---------|---------|---------|---------|---------|---------|
| Raw               | 1.65      | 0.20    | 2.11    | 0.76    | 0.20    | 0.13    | 0.56    |
| EFB B (EW1:7.5)   | 0.95      | 0.05    | 1.05    | 0.41    | 0.09    | 0.13    | 0.37    |
| EFB A (EW1:10)    | 0.54      | 0.02    | 1.02    | 0.19    | 0.12    | 0.10    | 0.36    |

Figure 6 Gas composition from different type of EFB samples

Figure 7 HHV of producer gas from EFB samples
4. Conclusions

In this study, pre-treatment of the EFB via leaching has a significant effect on the syngas composition and the energy content, by reducing the ash content and increasing the carbon content. The optimum condition used for the gasification of pre-treated EFB, based on the results of raw EFB gasification, is at 800°C and with 2.5 l/min of air flow rate. The highest value of HHV obtained in this study is 3.63 MJ/Nm³. Further investigation is required to enhance the gasifier performance, increasing the higher heating value for syngas for power generation.

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