Effect of combustion and nitrogen gas atmospheres on the torrefaction performance of oil palm frond leaves and stems

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Abstract. Torrefaction is a well-known method to thermally treats biomass at lower temperature range (200 to 300 °C) under inert atmosphere. However, the continuous supply of pure inert gas on large scale resist the commercialisation of this process. To investigate the effect of combustion gas (flue gas) on torrefaction performance of oil palm fronds leaves (OPFL) and stems (OPFS), both samples were torrefied at 200 °C for 30 min in a vertical tubular reactor under the atmosphere of combustion gas produced from wood pellets and nitrogen (inert) gas. The major components of combustion gas were nitrogen and carbon dioxide (total 76 vol% to 83 vol%) and the rest of the mixture contained oxygen, carbon monoxide and hydrogen. The effects of combustion gas atmosphere on the torrefaction performance of OPFL and OPFS including solid yield, calorific value, energy yield, proximate and ultimate compositions were investigated and compared with those of nitrogen atmosphere torrefaction. The combustion gas torrefaction resulted in lower solid yield and energy yield but with higher energy density (calorific value, carbon content) as compared to nitrogen torrefaction. Under combustion gas atmosphere, torrefaction of OPF stems gave higher solid yield (84.66 wt%) than OPF leaves (80.85 wt%) while solid yield of both samples under nitrogen atmosphere was almost same (88.02 wt% and 88.54 wt%). The increase in solid conversion under combustion atmosphere was caused by the partial oxidation took place in the presence of oxygen. Non-condensable gases at the outlet of the torrefaction reactor contained carbon dioxide and carbon monoxide.

1. Introduction
Malaysia is blessed with abundant biomass resources, especially oil palm waste biomass [1]. In 2016-2017, Malaysia was the world’s second largest producer of oil palm after Indonesia, producing 22.4 million tons of palm oil with 5.7 million hectares plantation area and 4.9 million hectares harvested area [2]. One of the important and huge waste of oil palm industry is oil palm fronds (OPF) generated about 26 million metric tonnes yearly on dry matter basis [3]. OPF have the great potential to be used as a renewable energy. However, to utilize these biomass waste as fuel efficiently, some of the drawbacks related to biomass must be addressed such as high moisture content and volatile matter, low energy density and hydrophilic nature [4]. Thermochemical processes (gasification, pyrolysis, co-combustion and torrefaction processes) are the effective ways to overcome these limitations and convert biomass into energy denser fuels with improved quality [5].
A pre-treatment of lignocellulosic biomass at lower temperatures (200–300 °C) in an inert atmosphere is known as torrefaction [4-8]. Torrefied biomass can be used as an appropriate feedstock for gasification, coal combustion and Fischer-Tropsch processes due to its higher calorific value and improved grindability than raw biomass [9]. During torrefaction process thermal activation of hemicellulose takes place and undergoes dehydration, deacetylation and depolymerisation in between the temperature range of 200 °C and 300 °C [10]. Previous researches mostly focused on the torrefaction of biomass under inert atmosphere and nitrogen gas from the cylinder had been used as an inert gas [11-14].

However, using nitrogen from the cylinder for torrefaction process is not economically feasible for industrialization of this process due to the cost of pure nitrogen gas. In order to overcome this problem researchers started studying on the effects of oxidative atmospheres such as air, oxygen, carbon dioxide and mixture of these gases on the torrefaction process with the motivation of using industrial flue gases into the torrefaction reactor [15-19]. In the above researches, all the gases had been supplied from the cylinders. Recently one study we have conducted torrefaction of empty fruit bunches and palm kernel shell in the atmosphere of real combustion gas with the conclusion that flue gases from the industrial boilers can be used in the torrefaction reactor without any significant problem may be due to the fact that nitrogen gas is the major component of flue gases [20-22]. In this study, the effect of combustion gas on the torrefaction performance of OPF leaves and stems was investigated. Both samples were torrefied for 30 minutes at low torrefaction temperature (200 °C) in the presence of combustion gas atmosphere which was generated by combusting wood pellets. For comparison, both samples were also torrefied at similar conditions under nitrogen gas (inert) atmosphere.

2. Experimental

2.1. Sample collection and preparation
Oil palm fronds (OPF) were collected from nearby oil palm mill (FELCRA Nasir Uddin Oil Palm Mill). First, they were washed with water to remove sand, dirt and unwanted material from the surface and left in a laboratory open atmosphere for two days for the removal of free moisture and then they were separated into two parts, one was the leaf part and the other was stem part. Both parts were chopped into 1 cm size, by mechanical knife and were dried in an air oven at 105 °C for 24 hours. The samples were then placed in an airtight containers until torrefaction experiments. The physiochemical properties of feedstocks are listed in Table 1. Each analysis was repeated three times and average results are presented.

| Table 1. Physiochemical properties of feedstocks (wt%). |
|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Moisture        | Ash            | Volatile matter| Fixed carbon   | Total carbon   | Hydrogen       | Nitrogen       | Oxygen         | HHV (MJ/kg)   |
| OPF leaves      | 7.24           | 4.79           | 82.16          | 5.80           | 48.52          | 6.95           | 1.77           | 38.17         | 18.83         |
| OPF stems       | 4.36           | 2.86           | 85.93          | 6.85           | 43.52          | 5.47           | 0.21           | 47.95         | 17.32         |

2.2. Torrefaction experiment
Torrefaction experiments of OPF leaves and OPF stems were conducted by using experimental setup presented in Figure 1 [20]. The setup contained two vertical tubular chambers made of stainless steel, one chamber for generating combustion gas (with internal diameter 10 cm and height 20 cm) and another chamber (with internal diameter 12 cm and height 15 cm) for conducting torrefaction experiment, both equipped with electric heater, respectively. Four thermocouples at different heights of the torrefaction reactor were used to measure the temperature at different depths of the biomass bed and one thermocouple was installed in the combustion chamber.

For the torrefaction under combustion gas atmosphere, first, 700 g to 800 g of biomass wood pellets were placed in the combustion chamber and were ignited manually. During burning of wood pellets, air was supplied from the bottom of chamber. The duration of combustion with flame took place for
approximately one hour. Once the flame went off and red glowing phase (stable combustion phase) appeared, the combustion chamber was closed tightly and thermocouple was inserted into the chamber and then combustion gas was directed into the torrefaction reactor, in which prescribed quantity of OPF leaves (100 g) or OPF stems (200 g) were kept and its temperature increased from room temperature to 200 °C with the heating rate of 4 °C/min, then kept at 200 °C for 30 minutes of process time. The combustion gas was continuously flowing during heating, processing and cooling phases. Throughout the experiment (from heating to cooling phase) the air was continuously supplied to the combustion chamber from the cylinder at 5 L/min which was controlled by mass flow controller. Temperature readings were recorded every 5 minutes during heating, processing and cooling phase. Combustion gas was sampled at 15 and 30 minutes of the processing and torrefaction gas was sampled at 10, 20 and 30 minutes of the processing time. After the process, torrefied samples were collected manually from the reactor, weighed and transferred into airtight containers until characterization. Liquid product was collected from two condensers fitted at the bottom of the reactor.

Torrefaction under nitrogen (inert) atmosphere was also performed by following the same procedure mentioned above except that, the pure nitrogen was supplied into the reactor instead of combustion gas, with the flow rate of 5 L/min.

![Figure 1. Schematic diagram of experimental setup](image)

2.3. Data processing and characterization

The mass of samples was measured before and after torrefaction, the calorific values (higher heating values) of samples were measured by bomb calorimeter (IKA C6000) according to ASTM D240-17. The moisture content, ash content, volatile matter contents and fixed carbon contents were determined before and after torrefaction in accordance with ASTM E 871-82, D 1102-84, E872-82 and fixed carbon was measured by difference. The total carbon, hydrogen and nitrogen contents (CHN) were measured before and after process by using CHN analyser (Series II CHNS/O Analyser 2400, Perkin Elmer) and oxygen content was calculated by subtracting the summation of total carbon, hydrogen, nitrogen and ash content.
X-ray diffraction (XRD) and X-ray fluorescence (XRF) analyses of samples were carried out by XRD diffractometer model PANalytical X’Pert 3 Powder (serial no DY5387) and XRF analyzer model S8 Tiger, respectively. The crystallinity index (CrI %) of untreated and treated OPF was calculated by using peak height method developed by Segal [23], the values of interlayer spacing (d002) is obtained from Bragg’s Equation and the crystallite size (L002) of the samples has been calculated by using Scherrer equation.

The compositions of combustion gas and non-condensable gases from torrefaction process were analysed by using gas chromatography with thermal conductivity detector (GC-TCD; Shimadzu GC-8A) with column packings of MS-5A and Porapak Q, respectively.

The solid yield, calorific value (CV) ratio and energy yield were calculated by using following equations 1, 2 and 3.

\[
Y_m (\text{wt} \%) = \frac{m_f}{m_i} \times 100
\]

\[
CV_{\text{ratio}} = \frac{CV_f}{CV_i} \times 100
\]

\[
Y_E = Y_m \times CV_{\text{ratio}}
\]

Nomenclatures of the equations are listed in Table 2.

| Abbreviation | Meaning |
|--------------|---------|
| \( Y_m \)   | Solid yield |
| \( m_f \)   | Mass of torrefied sample |
| \( m_i \)   | Initial mass of biomass sample |
| \( CV_f \)  | Calorific value of torrefied sample |
| \( CV_i \)  | Initial calorific value of biomass sample |
| \( CV_{\text{ratio}} \) | Calorific value ratio |
| \( Y_E \)   | Energy yield |

3. Results and discussion

3.1. Compositions of inlet combustion gas and outlet torrefaction gas

Compositions of inlet and outlet gases are listed in Table 3. Combustion gas generated from wood pellets consisted of nitrogen and carbon dioxide as the major components of the total mixture and rest contained low concentrations of oxygen, carbon monoxide and hydrogen. The presence of water vapors in combustion gas was considered to be negligible because combustion gas was directed into the torrefaction reactor only after the flame gone off (all gases burnt and hydrogen in wood pellets was almost consumed). Non-condensable gases produced at the outlet of the torrefaction reactor comprise of carbon dioxide as a major component and a trace of carbon monoxide. Carbon dioxide and carbon monoxide produced were due to the decarboxylation and decarbonylation reaction of the acid groups in biomass which remove
carboxyl group and release carbon dioxide [4, 5, 21], as well as partial combustion of OPF due to oxidation by remaining oxygen [20].

Table 3. Compositions (vol %) of gases at inlet and outlet of the reactor for OPFL and OPFS torrefaction.

| Gas | OPF Leaves | OPF Stems |
|-----|------------|-----------|
|     | Inlet 15 min | Inlet 30 min | Outlet 10 min | Outlet 20 min | Outlet 30 min | Inlet 15 min | Inlet 30 min | Outlet 10 min | Outlet 20 min | Outlet 30 min |
| N₂  | 67.08       | 66.92      | 66.2          | 68.69         | 65.55         | 66.89        | 68.48        | 65.6          | 66.82         | 55.99         |
| H₂  | 0.39        | 0.24       | 0.91          | 0.50          | 0.48          | 0.50         | 0.24         | 0.44          | 0.29          | 0.23          |
| O₂  | 1.98        | 5.35       | 1.25          | 5.68          | 2.90          | 1.49         | 6.12         | 1.49          | 2.56          | 2.44          |
| CO₂ | 16.21       | 13.27      | 15.66         | 15.01         | 15.76         | 16.50        | 12.67        | 16.67         | 16.20         | 17.25         |
| CO  | 3.87        | 3.12       | 3.07          | 2.90          | 4.7           | 5.41         | 0.96         | 2.39          | 2.31          | 2.62          |

3.2. Torrefaction yields

Figure 2 shows the effect of torrefaction atmosphere on the solid yield, energy yield and CV ratio of OPF leaves and stems. As it can be seen that solid yield during the torrefaction under combustion gas atmosphere is lower as compared to inert atmosphere and the same trend was observed for both raw materials (OPF stems and OPF leaves) in the present study. This is because during torrefaction under inert atmosphere, dehydration and devolatilization of hemicellulose take place [10].

According to Sellappah et al. [21] the presence of oxygen in combustion gas leads to the partial oxidation of lignocellulosic biomass which results in higher mass loss than inert atmosphere torrefaction. Similar trend was observed for the torrefaction of empty fruit bunches (EFB) in the presence of combustion gas in previous studies [20, 21].

The significant parameters of torrefaction process are calorific value and energy yield. As shown in Figure 2 the calorific value ratio (%) of combustion gas torrefied samples (104.14 and 110.53) are greater than inert gas torrefied samples (102.22 and 102.87) for both raw materials and energy yield is lower in combustion atmosphere torrefaction (84.19 % and 93.58 %) than in inert atmosphere torrefaction (89.99 % and 95.51 %). The energy density of torrefied samples in combustion atmosphere is greater due to the removal of more volatile matters because of additional oxidation took place in combustion atmosphere which increased the severity of torrefaction and energy yield decreased due to the increase of solid conversion [20].
Figure 2. Effect of torrefaction atmosphere on the solid yield, liquid yield, gas yield, energy yield and CV

3.3. Proximate and ultimate analysis

Figure 3 presents the effect of torrefaction atmosphere on proximate and ultimate analysis of samples. It can be seen in the figures that fixed carbon increased significantly after torrefaction. The fixed carbon and total carbon contents in combustion torrefied samples are higher than inert torrefied samples. This is due to the removal of more volatile matters due to the partial oxidation in the presence of combustion gases. The reduction in moisture contents, volatile matter, hydrogen and oxygen content has been observed after torrefaction due to the dehydration and devolatilization occurred during torrefaction process.

Figure 3. Proximate and ultimate analysis of raw and torrefied OPFL and OPFS

However, combustion torrefaction increased the heating value slightly higher (from 18.83 to 19.81 MJ/kg for OPFL and from 17.32 to 19.14 MJ/kg for OPFS) as compared to nitrogen torrefaction (19.25 MJ/kg...
for OPFL and 18.68 MJ/kg for OPFS) showing that combustion gas atmosphere improved the energy density.

3.4. X-Ray Fluorescence Spectroscopy and X-Ray Diffraction analysis

XRF analysis of ash shows that Ca, Si, K, P and Mg are the major components of the ashes (making up 95.38 wt. % for OPFL and 97.58 wt. % for OPFS) prepared from OPFL and OPFS. However, OPFS shows higher amount of Ca (73.50 %) and lower amount of Si (3.72 %) than OPFL with 54.17 % Ca and 21.33 % Si, respectively. The crystallinity index (CrI) of raw OPF and torrefied OPF are 62.04 % (raw), 47.25 % (torrefied in combustion gas) and 43.13 % (torrefied in nitrogen gas). Interplanar spacing decreased from 4.39 Å (raw OPF) to 4.00 Å (combustion torrefied) and 3.99 Å (nitrogen torrefied). Crystallite size decreased from 37.05 nm (raw OPF) to 34.31 nm (nitrogen torrefied) and 32.74 nm (combustion torrefied) respectively.

4. Conclusion

Oil palm fronds stems and leaves were torrefied at lower temperature (200 °C) in combustion and nitrogen gas atmospheres for 30 min of process time. Results shows that torrefaction atmosphere has also impact on its performance. Torrefaction under combustion atmosphere increased the severity of torrefaction (more solid conversion) and this effect may be due to the partial oxidation caused by oxygen and Boudard reaction due to the presence of carbon dioxide in the combustion gas. Torrefied biomass under combustion showed higher calorific value (carbon contents), fixed carbon and lower hydrogen and oxygen contents due to the additional decompositions of biomass as compared to nitrogen torrefied biomass. Furthermore, XRD results indicates that crystallinity index, interplanar spacing and crystallite size of samples declined after torrefaction. A thorough conclusion from this study is that the flue gases from the industrial boilers can be utilized in the torrefaction reactor instead of pure nitrogen gas to make process economically feasible and commercialization.

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References

[1] Umair M S, Urmee T and Jenning P 2018 A policy framework and industry roadmap model for sustainable oil palm biomass electricity generation in Malaysia Renew. Energy 128 275-284
[2] Kusumaningtyas R and Gelder J 2017 Towards responsible and inclusive financing of the palm oil sector CIFOR occas. paper 175
[3] Zahari M W, Hassan O A, Wong H K and Liang J B 2003 Utilization of oil palm frond-based diets for beef and dairy production in Malaysia Asian-Australas J. Anim. Sci. 16 4 625-634
[4] Tumuluru J S, Sokhansanj S, Wright C T, Hess J R and Boardman R D 2011 A review on biomass torrefaction process and product properties for energy applications Ind. Biotechnol. 7 (5) 384-401
[5] Eseltine D, Thanapal S, Annamalai K and Ranjan D 2013 Torrefaction of woody biomass (Juniper and Mesquite) using inert and non-inert gases "Fuel" 113 379-388
[6] Chen D, Gao A, Cen K, Zhang J, Cao X and Ma Z 2018 Investigation of biomass torrefaction based on three major components: Hemicellulose, cellulose, and lignin Energ. convers. manage. 169 228-237
[7] Wang L, Rajnai E B, Skreiberg O and Khalil R 2018 Effect of torrefaction on physiochemical characteristics and grindability of stem wood, stump and bark Appl. Energy 227 137-148
[8] Zhang C, Ho S-H, Chen WH, Xie Y, Liu Z and Chang JS 2018 Torrefaction performance and energy usage of biomass wastes and their correlations with torrefaction severity index Appl. Energy 220 598-604
[9] Ciolkosz D and Wallace R 2011 A review of torrefaction for bioenergy feedstock production Biofuel Bioprod. Biorefin. 5 (3) 317-329
[10] Fisher T, Hajaligol M, Waymack B and Kellogg D 2002 Pyrolysis behavior and kinetics of biomass derived materials J. Anal. Appl. Pyrol. 62 (2) 331-349.

[11] Bridgeman T, Jones J, Williams A and Waldron DJ 2010 An investigation of the grindability of two torrefied energy crops Fuel 89 (12) 3911-3918

[12] Chen WH and Kuo PC 2010 A study on torrefaction of various biomass materials and its impact on lignocellulosic structure simulated by a thermogravimetry Energy 35 (6) 2580-2586

[13] Sabil KM, Aziz MA, Lal B and Uemura Y 2013 Effects of torrefaction on the physiochemical properties of oil palm empty fruit bunches, mesocarp fiber and kernel shell Biomass Bioenerg 56 351-360

[14] Uemura Y, Omar W N, Tsutsui T and Yusup S 2011 Torrefaction of oil palm wastes Fuel 90 (8) 2585-2591

[15] Chen WH, Lu KM, Liu SH, Tsai CM Lee WJ and Lin TC 2013 Biomass torrefaction characteristics in inert and oxidative atmospheres at various superficial velocities Bioresour. Technol. 146 152-160

[16] Li MF, Li X, Bian J, Xu JK, Yang S and Sun RC 2015 Influence of temperature on bamboo torrefaction under carbon dioxide atmosphere Ind. Crop. Prod. 76 149-157

[17] Chen WH, Lu KM, Lee WJ, Liu SH and Lin TC 2014 Non-oxidative and oxidative torrefaction characterization and SEM observations of fibrous and ligneous biomass Appl. Energy 114 104-113

[18] Chen WH, Zhuang YQ, Liu SH , Juan T and Tsai CM 2016 Product characteristics from the torrefaction of oil palm fiber pellets in inert and oxidative atmospheres Bioresour. Technol. 199 367-374

[19] Uemura Y, Saadon S, Osman N, Mansor N and Tanoue K 2015 Torrefaction of oil palm kernel shell in the presence of oxygen and carbon dioxide Fuel 144 171-179

[20] Uemura Y, Sellappah V, Trinh TH, Hassan S and Tanoue K 2017 Torrefaction of empty fruit bunches under biomass combustion gas atmosphere Bioresour. Technol. 243 107-117

[21] Sellappah V, Uemura Y, Hassan S, Sulaiman MH and Lam MK 2016 Torrefaction of empty fruit bunch in the presence of combustion gas Proc. Eng. 148 750-757

[22] Uemura Y, Sellappah V, Trinh TH, Komiyama M, Hassan S and Tanoue K 2018 Improvement of energy density and energy yield of oil palm biomass by torrefaction in combustion gas Mat. Sci. Eng. 458 012061

[23] Park s, Baker JO, Himmel M E, Parilla P A and Johnson DK 2010 Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulase performance Biotechnol. biofuel. 3 (1)10