Torrefaction in the Presence of Oxygen and Carbon Dioxide: The Effect on Yield of Oil Palm Kernel Shell

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Abstract

Torrefaction refers to a thermochemical treatment that reduces the moisture content of biomass and increases its energy density by removing water and lower energy volatiles. Torrefaction process requires mild treatment temperature between 200 to 300 °C in the absence of oxygen (inert atmosphere). Through torrefaction, biomass transformed into a char-like solid with higher value than the raw biomass. Industries found it applicable for the torrefied biomass to be co-fired with coal in power plants because of the close similarity in properties. The torrefied biomass can also be used as feedstock for entrained-flow gasifier, or for residential heating. During torrefaction, a continuous supply of nitrogen to create the needed inert state incurs certain cash flow to the torrefaction plant; meanwhile the nitrogen price is depending on the volatile prices of natural gas that is currently suffered from depletion. The alternative of this problem is to utilize flue gas as a replacement of the nitrogen in parallel with the fact that nitrogen is a major composition of flue gas. A fundamental study is needed to support the idea, for that reason this paper studied how the behaviour of torrefaction diverged when the process was carried out in the presence of oxygen and carbon dioxide. The chosen biomass is oil palm kernel shell (PKS) due to its abundance in Malaysia. The torrefactionis carried out 250 °C for 30 min. In comparison to the solid yield of torrefied PKS in inert torrefaction, the solid yield in oxygen and carbon dioxide torrefaction is practically unaffected by the non-inert gases. Liquid yield is almost similar in each torrefaction condition; however the gas yield in carbon dioxide torrefaction is produced intensely compared to the gas yield in oxygen torrefaction.

Keywords: Torrefaction; Biomass; Inert; Flue gas; Mass yield

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Introduction

Torrefaction refers to a thermal pre-treatment technology to improve the characteristics of lignocellulosic biomass into an attractive biofuel. Torrefaction removes the oxygen content; hence the final solid product is torrefied biomass with lower O/C ratio than the untreated biomass that can be used for combustion and gasification [1]. As the fossil fuels depleted, the future of renewable energy has been averted into the direction of biomass because of its abundance and low cost. In Malaysia, the biomass from oil palm wastes such as mesocarp fibre, kernel shell, empty fruit bunch, fronds and trunk are readily available. The stability of climate changes in Malaysia with high rainfall and sunlight intensity enables the annual generation of oil palm wastes in large quantity. However, generally there are a few characteristics of raw biomass that hinder its performance as a biofuel. The moisture contained in raw biomass is high, whereas the energy density of the raw biomass is low compared to that of fossil fuels, thus restrict the prospect for industrial applications. The biomass cannot be stored or transport for a long haulage because of the hygroscopic nature [2]. Torrefaction helps to remove the moisture and low weight organic volatiles, thus at the end of the process the torrefied biomass is energy denser with high fixed carbon content [3].

In essence, there are five important phases involved in torrefaction. The first phase consists of free and bound water extraction from biomass at the boiling point of water (105 °C) that associated to the drying of biomass. The second phase is irreversible biomass degradation occurs at temperatures ranging from 100 to 250 °C. The third phase, which occurs between about 250 and 330 °C, usually involves the total destruction of most reactive component of lignocellulosic biomass, hemicelluloses. The destruction of cellulose occurs during the fourth phase, between about 330 and 370 °C. Lignin, being the most resistant lignicellulosic component, is only degrades at high temperature above 350 °C [4].

Torrefaction is conducted in a temperature range of 200 to 300 °C under an inert atmosphere. A study on the effect of moisture content on the product yield distribution of biomass has revealed that more mass and energy losses occurred in high moisture content sample [5]. The mass and energy yields of biomass decrease with the increase in the operating temperature and residence time, however, the temperature had a stronger impact on the increase in the energy density of the torrefied biomass [5-8].

Previous researchers’ work is mostly focused on the effect of temperature and residence time on various type of biomass, however there is insufficient data to support the findings on non-inert atmosphere influence to the performance of torrefaction. Such studies on torrefaction of biomass in the presence of oxygen [9, 10] and carbon dioxide (CO₂) will provide an opportunity for a lower pretreatment cost of biomass. In current study, the author’s intention is to model the incorporation of flue gas into the torrefaction treatment by simulating the composition of the flue gas. Typical composition of flue gas consists of 76 % (by volume) nitrogen, 6 – 14 % oxygen, 6 – 13 % CO₂ and traces of water, carbon monoxide and hydrogen [12]. Thus, the objective of this study is to investigate the effect of oxygen and CO₂ co-feeding (non-inert) with nitrogen (inert) on the torrefaction of biomass with product yield as indicator. The nitrogen, oxygen and CO₂ are supplied from separate sources and the pre-determined concentration for each gas is controlled.

1. Experimental method

Fig. 1 illustrates the schematic diagram of the torrefaction reactor setup. The biomass in interest is palm kernel shell (particle size 0.5 to 1 cm; moisture content 10.0 wt %; ash content 1.82 wt %) collected from an oil palm mill in Perak state, Malaysia. The palm kernel shell (PKS) sample has been dried in oven at 105 °C for 24 h prior to the experiment. The torrefaction is carried out in a stainless steel vertical tubular reactor (length 56 cm; diameter 2.71 cm). The experiment consists of three parts; the first part is inert torrefaction that serves as control. In inert torrefaction only nitrogen gas is flowed into the reactor. The second part is oxygen torrefaction, in which 3, 9 and 15 vol % of oxygen is co-feed with the nitrogen and flowed into the reactor. The third part, CO₂ torrefaction, 9, 12 and 15 vol % of CO₂ is co-feed with the nitrogen. The nitrogen and CO₂ are supplied from cylinder tanks while oxygen is supplied from compressed air source. The concentration of oxygen and CO₂ co-feed is determined from the typical composition of flue gas. The flowrate of the mixture gases is 30 ml/min and the amount of sample torrefied in each experiment is 3 g. The sample is heated up to desired treatment temperature (250 °C) at a heating rate of 10 °C/min, and once the temperature is achieved the reaction is allowed to take place for 30 min. The biomass is cooled
down to room temperature before the torrefied biomass (solid char) is retrieved and weighted. The gas product from the decomposition reaction of biomass is channeled to the bottom of reactor, passed through a condenser in ice bath at -5 °C. Condensable gas (liquid product) is collected from the condenser while the non-condensable gas (gas product) is collected manually every 15 min along the experiment and analyzed in Gas Chromatogram with Thermal Conductivity Detector (GC-TCD).

2. Results and Discussion

2.1. The influence of oxygen existence in torrefaction of biomass

The yield distribution of PKS in Fig. 2 provides an understanding on the behavior of biomass torrefied in the presence of oxygen in contrast to torrefaction in total inert. The yield of solid, condensable and non-condensable substances is calculated from Equation (1);

\[
Y_m = \frac{m_t}{m_b} \times 100
\]

where \(Y_m\) is yield (by mass), \(m_t\) is mass of product after torrefaction and \(m_b\) is mass of untreated/untorrefied biomass. It can be observed from Fig. 2 that there is a minor decrease of solid yield (2 %) as the oxygen concentration is increased from inert to 15 vol %, in comparison to the solid yield in inert torrefaction. On the other hand, the yields of condensable and non-condensable gas are increased with oxygen concentration, with 22 % increment in the latter and only 3 % in the former. This product distribution is a result of competition between charring and devolitization reactions as heat is supplied to the biomass [13]. During the decomposition reaction, the conversion of biomass into solid, liquid and gas product is varied by biomass properties and operating conditions. PKS generally contains 26 wt % hemicellulose, 22 wt % cellulose and 46 wt % lignin [14], and it is well-established from literature that biomass decomposition in torrefaction is highly dependent on temperature. Because cellulose is normally decomposes at the above 330 °C thus, it is anticipated that at the end of torrefaction the solid retained is approximately 80 % (Fig. 2). The conversion of the PKS into volatiles might be mostly due to the decomposition of hemicellulose. In this study the treatment temperature is kept constant at 250 °C, and so manipulating the oxygen concentration appears not to
influence the yield of products significantly. However, it can be noticed that the solid yield in oxygen torrefaction is lower than inert torrefaction, that may be attributed to the oxidation reaction of biomass [9]. The result in Fig. 2 reveal that the effect of oxygen on the solid yield of PKS is almost negligence. The ratio of the formation of solid, condensable and non-condensable substances can be formulated as 8:1:1.

![Graph showing yield distribution between torrefaction in inert environment and in the presence of oxygen at 250 °C.](image)

Fig. 2: Comparison of yield distribution between torrefaction in inert environment and in the presence of oxygen at 250 °C.

Among the principle gases produced from torrefaction include carbon dioxide, carbon monoxide and methane, in most cases of biomass torrefaction CO₂ is majorly produced as compared to other gases [7]. The CO₂ is formed as a result of decarboxylation and depolymerization of acid groups in biomass [15]. In Fig. 3, the evolution profile for CO₂ (in mol/min) throughout the experiment is presented. The first 40 min belong to the heating stage of biomass to the desired temperature (250 °C) and a shallow production of CO₂ is observed at this stage. The torrefaction reaction is then allowed to take place until 70 min, and the production of CO₂ is increased exponentially along this stage. After torrefaction reaction time, there is still CO₂ produced during the cooling stage. A preliminary observation from Fig. 3 is that the production of CO₂ is almost similar for both inert and oxygen torrefaction, judging from the curve trend and the position of the highest peak.

![Graph showing CO₂ formation rate vs time for different oxygen concentrations.](image)
An integration of area under curve enabled us to obtain the total mol of CO$_2$ produced, and the result is summarized in Table 1. It can be observed from the table that the total mol of CO$_2$ produced is increased with increasing oxygen concentration. In comparison to inert, at 3vol % oxygen the CO$_2$ is increased by one half, while at 15 vol % oxygen the CO$_2$ production is almost doubled. This observation compliments the finding in Fig. 2, in which the large mass loss in 15 vol % oxygen is attributed to the oxidation of biomass, hence explained the lowest solid mass retained.

<table>
<thead>
<tr>
<th>Oxygen concentration [vol %]</th>
<th>Amount of CO$_2$ [x10$^{-3}$mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inert</td>
<td>1.20</td>
</tr>
<tr>
<td>3</td>
<td>1.80</td>
</tr>
<tr>
<td>9</td>
<td>2.06</td>
</tr>
<tr>
<td>15</td>
<td>2.27</td>
</tr>
</tbody>
</table>

2.2. The influence of carbon dioxide existence in torrefaction of biomass

The effect of CO$_2$ presence in torrefaction was investigated to strengthen the objective of this study. The effect of oxygen and CO$_2$ is not done simultaneously to avoid complexities in understanding the behavior of non-inert torrefaction. Yield distribution after CO$_2$ torrefaction in Fig. 4 shows a slight decrease in solid yield, by approximately 3 %, when the concentration of CO$_2$ is increased from 9 to 15 vol %. This may be because CO$_2$ does not influence the mass change of thermal degradation of biomass at a heating rate 10 °C/min. The influence of CO$_2$ is limited to the reaction between volatiles evolved from the degradation of cellulose and CO$_2$ feed gas [11]. In contrast to oxygen torrefaction (Fig. 2), the yield of condensable substance is decreased with increasing CO$_2$ concentration (22 %), but the non-condensable substance is increased intensely (45 %). This finding is rather surprising, and an inference can be made from this observation: CO$_2$ presence suppressed the formation of liquid and boosted the generation of volatiles compound [11]. The ratio of the formation of solid, condensable and non-condensable substances can be estimated as 8:0.5:1.5.
The evolution profile of CO\textsubscript{2} for the carbon dioxide torrefaction is plotted in Fig. 5. Note that the CO\textsubscript{2} formation rate shown in the figure is merely the one produced as a gas product and did not include CO\textsubscript{2} feed gas. It was observed in the Fig. 5 that the highest peak is clearly revealed in each evolution profile occurred at approximately 55 min. At this particular period, it is in the middle of torrefaction stage. Meanwhile in Fig. 3, the highest peak location is rather undefined, and the distribution of the plot is flat. The formation rate of CO\textsubscript{2} in oxygen torrefaction does not exceed 0.6x10^{-4}mol/min, meanwhile in CO\textsubscript{2}torrefaction the highest formation rate is observed at 2x10^{-4}mol/min.

![Fig. 5. Evolution profiles of CO\textsubscript{2} in gas product in inert and carbon dioxide torrefaction at 250 °C.](image)

The result of integration under curve confirms the finding in Fig. 5. At 9 vol % CO\textsubscript{2}, the CO\textsubscript{2} production is almost doubled from the inert torrefaction, while at 15 vol % CO\textsubscript{2}, the CO\textsubscript{2} is produced by a factor of 2.5. The increase in the yield of non-condensable substance in Fig. 4 may be attributed to the high formation of CO\textsubscript{2} gas product hence explained the lowest solid yield acquired in 15 vol % CO\textsubscript{2}.

<table>
<thead>
<tr>
<th>Carbon dioxide concentration [vol %]</th>
<th>Amount of CO\textsubscript{2} [x10^{-3}mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inert</td>
<td>1.20</td>
</tr>
<tr>
<td>9</td>
<td>2.10</td>
</tr>
<tr>
<td>12</td>
<td>2.20</td>
</tr>
<tr>
<td>15</td>
<td>3.00</td>
</tr>
</tbody>
</table>

Table 3 shows the fraction of CO\textsubscript{2} product in total gas yield from oxygen and CO\textsubscript{2}torrefaction, with regards to concentration. In 9 vol % co-feed torrefaction, the percentage of CO\textsubscript{2} product in CO\textsubscript{2}torrefaction is higher than that in oxygen torrefaction, but the difference is minor. Meanwhile in both 15 vol % co-feed torrefaction, the CO\textsubscript{2}-percentage is approximately same. This consistency indicates that the type of co-feed gas does not influence the generation or reduction of CO\textsubscript{2} product in torrefaction, but slightly influenced by the concentration. However, at higher temperature (above 700 °C) such as that incorporated in pyrolysis, the effect of co-feed gas may be different.
Table 3. Fraction of CO₂ from total gas yielded from torrefaction

<table>
<thead>
<tr>
<th>Concentration [vol %]</th>
<th>Co-feed gas</th>
<th>Amount of CO₂ evolved [mol]</th>
<th>Total weight [g]</th>
<th>CO₂ yield [%]</th>
<th>CO₂ in total gas yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>Oxygen</td>
<td>2.06</td>
<td>0.07</td>
<td>2.31</td>
<td>23 %</td>
</tr>
<tr>
<td></td>
<td>CO₂</td>
<td>2.10</td>
<td>0.09</td>
<td>2.94</td>
<td>27 %</td>
</tr>
<tr>
<td>15</td>
<td>Oxygen</td>
<td>2.27</td>
<td>0.08</td>
<td>2.84</td>
<td>29 %</td>
</tr>
<tr>
<td></td>
<td>CO₂</td>
<td>3.00</td>
<td>0.10</td>
<td>3.25</td>
<td>30 %</td>
</tr>
</tbody>
</table>

4. Conclusion

The effect of non-inert atmospheres on the torrefaction of palm kernel shell have been investigated and compared with inert torrefaction. The concentration of oxygen and CO₂ below 15 vol % has been chosen as the manipulated variables by co-feeding with nitrogen to simulate the composition of flue gas. The existence of oxygen and CO₂ in torrefaction has caused a minor decrease in solid yield (by 2-3 %). The difference of solid yield in oxygen torrefaction may be attributed to the oxidation reaction. The liquid and gas yield of oxygen torrefaction increased with increasing oxygen concentration, with ratio of liquid to gas 1:1. On the other hand, the gas yield in CO₂ torrefaction is increased intensely. The enhanced generation of the gas suppressed the formation of liquid yield, making the ratio of liquid to gas shift to 1:2. Total area under the curve shows that the CO₂ product in CO₂ torrefaction exceeds the CO₂ product in oxygen torrefaction, indicates enhanced biomass thermal degradation. However, in both torrefaction conditions, the fraction of CO₂ product in total gas yielded is similar. A thorough conclusion from this study is that there is a limited influence of non-inert environment to the torrefaction behavior of biomass. The finding may contribute to the effort of lowering the cost of torrefaction by incorporating flue gas in torrefaction process.

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References


