The Potential of CO₂ Torrefaction as Biomass Pre-Treatment Method

R. Abdul Rasid^{*} and M. H. M. Yusoff

Faculty of Chemical Engineering and Natural Resources, Universiti Malaysia Pahang, Gambang - 26300, Pahang, Malaysia; ruwaida@ump.edu.my

Abstract

Background/Objectives: The aim of this study is to evaluate the effect of carbon dioxide (CO_2) for potentially improving the torrefaction of the empty fruit bunch (EFB), whereby conventional torrefaction is usually performed in an inert environment. **Methods/Statistical Analysis**: The experiment was carried out in a vertical tubular reactor, for various CO_2 concentrations (0%, 10%, 15% and 21%) at two (2) different temperatures; 240°C representing the mild torrefaction and at 280°C representing the severe torrefaction condition. Additionally, the impact of torrefaction was also evaluated at 15 and 30 minutes. **Findings**: It was observed that the appearance of the torrefied EFB tends be darker at the severe torrefaction temperature due to carbonization. The mass yield emits distinctive trends, whereby at 30 minutes residence time, the mass yield was decreased to less than 30% of the initial weight as the concentration of CO_2 was increased. The moisture content was improved from 7.22% down to 4.92% at the mild torrefaction while similar trend was observed for the severe torrefaction condition, as the concentration of CO_2 was increased. **Application/Improvements**: This suggest the potential of utilizing CO_2 in the torrefaction process is beneficial and should be explored further to improve the properties of biomass for energy application.

Keywords: Biomass Pre-Treatment, Carbon dioxide, Oxidative Torrefaction, Torrefaction

Introduction

Biomass such as the Empty Fruit Bunch (EFB) is one of the main solid wastes from the palm oil industry and has the potential to be utilized as a renewable energy. The use of biomass can reduce the emission of greenhouse gases released by conventional fossil-based fuel. Torrefaction process is the process where the biomass is thermally treated in temperature between 200 to 300°C under atmospheric conditions without the presence of any types of oxidizer¹. By using the torrefaction process, the properties of biomass can be improved in term of its energy density and moisture content comparable to the conventional coal. Torrefaction also partially decomposes the organic constituents of the biomass².

Carbon dioxide (CO_2) is one of the greenhouse gases that is released into the environment during energy production process such as combustion and gasification of

*Author for correspondence

solid fuels. Hot gases produced from boiler exhaust that has concentrated amount of CO_2 in it, offers an alternative option to be used as the biomass pre-treatment medium. There have been several studies on torrefaction of different types of woody biomasses such as agricultural residues and herbaceous energy crops include pine sawdust³, forest residues⁴, tomato peels⁵ and corn stover⁶. Conventional torrefaction is usually carried out in an inert environment⁷. It is only recently that non-conventional torrefaction is explored through the presence of oxidative medium such as oxygen $(O_2)^8$, combination of O_2 and CO_2^9 and wet torrefaction¹⁰.

In the present study, the effect of CO_2 concentration, the torrefaction temperature and residence time on the mass yield of EFB has been studied and the characteristics of untreated and treated empty fruit bunches have been evaluated.

2. Materials and Methods

2.1 Samples

The EFB was obtained from an oil palm plantation in Lepar, Pahang. EFB is the residue generated at the thresher, where fruits are removed from fresh fruit bunches. The raw EFB was initially sun-dried. They were subsequently oven-dried in the lab. For the drying process, the EFB samples were weighed and placed in a tray. Then, the EFB samples were dried in an oven at the temperature of 65°C for 24 hours to provide a basis for the following experiments. After the drying process, the samples were grounded and sieved using the mechanical grinder and the sieve shaker respectively. The samples were stored until needed.

The experimental set-up consists of N_2 and O_2 cylinders, a vertical stainless-steel tubular reactor equipped with an electrically heated furnace and a condenser. The volumetric flow rate of the gases was controlled by electronic mass flow controllers. A 3 g of biomass sample was weighed and placed in the tubular reactor. The reactor was placed at the centre of the furnace. The heating rate of 10 °C/ min was applied until the desired torrefaction temperature is reached at240°C and 280°C and kept constant at the desired residence time. Afterwards, the furnace was turned off and is left to cool to ambient temperature. The torrefied sample was recovered, weighted and stored until further analysis. The experiments were repeated for difference CO_2 concentrations. Each sets of experiments were repeated to ensure its consistency.

2.2 Analysis

The most important properties that needs to be analysed are, among others, the Proximate Analysis (PA), the Ultimate Analysis (UA) and its mass yield/loss. The PA of the EFB was done to quantify its moisture, ash, volatiles and fixed carbon contents, through the Thermo Gravimetric Analyser (TGA) (Model PerkinElmer Pyris 1) available in the FKKSA Lab, UMP.

The ultimate analysis was done to determine the elemental composition of the EFB, which includes carbon, hydrogen, nitrogen and sulphur, while oxygen may be determined by the difference. The mass yield after the torrefaction process may be calculated from equation (1) as follows:

$$y = \frac{m_f}{m_i} \times 100\% \tag{1}$$

Where *y* is the mass yield, m_f and m_i are the final and initial weight of the biomass, respectively, before and after the torrefaction process. The surface structure of the biomass, raw and treated may be studied and analysed through the Scanning Electron Microscope (SEM), available in Central Lab, UMP. The SEM images of the torrefied samples and raw biomass can be used to study the presence of pores on the samples torrefied under different conditions². The images were obtained at a magnification of 100x, 500x, 1000x, and 3000× to identify the pores formed on the samples when using different torrefaction mediums.

In this study, two different torrefaction temperatures of 240°C and 280°C were considered. Since the effect of the CO_2 presence was of interest, its concentration in N₂was evaluated. Two different torrefaction times of 15 and 30 minutes were tested to see if the presence of CO_2 wound reduce the required residence time. Table 1 summarises the raw EFB characteristics. According to the proximate analysis, moisture, VM, FC and ash content in the raw EFB are 8.41 wt.%, 57.45 wt.%, 29.90 wt.% and 4.24 wt.% respectively.

Table 1	. Raw	EFB	Anal	ysis
---------	-------	-----	------	------

Analysis	Value	
Proximate analysis (wt. %)		
Moisture	8.411	
Volatile matter (VM)	57.45	
Fixed Carbon (FC)	29.9	
Ash	4.24	
Elemental analysis (wt. %)		
С	46.71	
Н	7.335	
Ν	1.22	
0	44.658	
HHV (MJ/kg)	40.43	
Particle density (g/cm ³)	1.3075	

3. Results and Discussion

3.1 Appearance of the Torrefied Biomass

In this study, the EFB was torrefied at different concentration of CO_2 at temperature of 240°C and 280°C. Figure 1 illustrates the raw sample as well as the torrefied samples appearance. The color of EFB was initially yellowish/ brownish in appearance, tending towards black as the







(b) 100% N₂, 280°C



(c) 10% CO₂, 280°C **Figure 1.** Biomass appearance.

temperature increases. This finding is consistent as in the literature¹¹⁻¹³. Especially at higher torrefaction temperature, it is thought that the appearance of the torrefied biomass was mainly due to light carbonization¹⁴.



Figure 2. Mass yield at 15 minutes residence time.

3.1 The Effect of Temperature and CO₂ Concentration on Mass Yield

Figure 2 and Figure 3 presents the effect of mass yield at carbon dioxide concentrations of 10%, 15% and 21%, for residence time of 15 minutes and 30 minutes respec-



(d) 21% CO₂, 280°C



Figure 3. Mass yield at 30 minutes residence time.

tively. It was determined that for the 15 minutes residence time, the higher torrefaction temperature yields higher mass. This is evident in Figure 2, at 280°C, the mass yield is about 40%. Of the three (3) CO_2 concentration tested, 15% was proved to be the most optimum concentration mix that yields the highest percentage of mass yield. On the other hand, at longer residence time, it was found that the increase in the CO_2 concentration was detrimental towards the mass yield, where at 10% CO_2 concentration yields the highest percentage of mass yield of 40%. Overall, it was shown that the presence of CO_2 would be able to reduce the residence time needed to achieve similar mass yield, hence reducing the energy requirement and consumption needed to power up the torrefaction process.



Figure 4. Elemental analysis of the torrefied biomass at 240°C.



Figure 5. Elemental analysis of the torrefied biomass at 280°C.

3.2 The Fuel Characteristic of Torrefied Biomass

The torrefied biomass as solid fuel was observed in term of its proximate and ultimate analysis. The focus for the proximate analysis would be to observe the changes in its moisture content, which would be important as untreated biomass are high in moisture content and direct application would reduce in the subsequent process efficiency. It was observed that the moisture content of torrefied biomass was generally lower at higher torrefaction temperature. In addition, the concentration of CO₂ had also a positive impact in reducing the moisture content of the biomass, since the increased CO₂ concentration would cause the moisture content to be reduced. The fixed carbon content was also observed to be decreasing with the increased in CO₂ content. This may suggest that some of the carbons as well as the volatiles were released during the torrefaction process.

The evolution of the elements in the torrefied solid is represented by Figure 4 and 5 at 240°C and 280°C respectively. It is observed that there is an improvement with regards to the carbon content of all the samples when compared to raw untreated biomass. The presence of CO_2 during the process was also had a positive influence, and it is more evident at higher torrefaction temperature, as can be shown in Figure 5.

3.3 The Surface Structure of the Biomass

SEM analysis provides information about the structural changes that takes place on the raw biomass char during the torrefaction processes. Figure 6 shows the SEM analysis results of raw torrefied char particles at different temperature, 240°C and 280°C respectively. It was



a) Raw b) 240°C c) 280°C Figure 6. SEM analysis for the raw and torrefied EFB at 240oC and 280oC, 10% CO2 in 30 min at 3.00 K magnification.

observed that the application of temperature to the raw EFB causes the chemical bonds to break thermally and this, in turn, breaks the fibrous structure of the EFB and increases the pores in the char particles. The higher temperature apparently had the stronger effect as can be shown in Figure 6c.

4. Conclusion

The characteristic of torrefied EFB at the temperatures of 240°C and 280°C using N_2 and CO_2 as the carrier gases have been investigated and compared to that of the raw, untreated EFB. The results showed that the higher torrefaction temperature could improve the solid products properties. In addition, the presence of CO₂ in the gas carrier medium had also a positive influence in the matter. Compared to the conventional total inert environment with only N₂, additional CO₂ would be a better mixed carrier gas as found this this study, hence warrant for further investigations to improve the properties of the torrefied biomass. The International Conference on Fluids and Chemical Engineering (FluidsChE 2017) is the second in series with complete information on the official website¹⁵ and organised by The Center of Excellence for Advanced Research in Fluid Flow (CARIFF)¹⁶. The publications on products from natural resources, polymer technology, and pharmaceutical technology have been published as a special note in volume 217. The conference host being University Malaysia Pahang¹⁸ is the parent governing body.

5. Acknowledgement

This project was supported by the Ministry of Higher Education Malaysia (RDU140134) and Universiti Malaysia Pahang (RDU150366). The authors also thank the Faculty of Chemical Engineering and Natural Resources, Universiti Malaysia Pahang for providing the lab space to conduct the trials.

6. References

- Chen W-H, Cheng W-Y, Lu K-M, Huang Y-P. An evaluation on improvement of pulverized biomass property for solid fuel through torrefaction. Applied Energy. 2011; 3630–44. Crossref
- Prins MJ, Ptasinski KJ, Jansen FJ. Torrefaction of wood: Part 2. Analysis of Products. Journal of Analytical and Applied Pyrolysis. 2006; 77(1):35–40. Crossref

- Gong C, Huang J, Feng C, Wang G, Tabil L, Wang D. Effects and mechanism of ball milling on torrefaction of pine sawdust. Bioresource technology. 2016; 214:242–7. Crossref PMid:27136611
- Bach QV, Chen WH, Chu YS, Skreiberg O. Predictions of biochar yield and elemental composition during torrefaction of forest residues. Bioresource Technology. 2016; 215:239–46. Crossref PMid:27072788
- 5. Toscano G, Pizzi A, Pedretti EF, Rossini G, Ciceri G, Martignon G, Duca D. Torrefaction of tomato industry residues. Fuel. 2015; 143:89–97. Crossref
- 6. Tumuluru JS. Effect of process variables on the density and durability of the pellets made from high moisture corn stover. Biosystems Engineering. 2014; 119:44–57. Crossref
- Kaliyan N, Morey RV, Tiffany DG, Lee WF. Life cycle assessment of a corn stover torrefaction plant integrated with a corn ethanol plant and a coal fired power plant. Biomass and Bioenergy. 2014; 63:92–100. Crossref
- 8. Deng J, Wang G-J, Kuang J-H, Zhang Y-L, Luo Y-H. Pretreatment of agricultural residues for co-gasification via torrefaction. Journal of Analytical and Applied Pyrolysis. 2009; 86:331–7. Crossref
- Uemura Y, Omar W, Othman NA, Yusup S, Tsutsui T. Torrefaction of oil palm EFB in the presence of oxygen. Fuel. 2013; 156–60. Crossref
- Saadon S, Uemura Y, Mansor N. Torrefaction in the Presence of Oxygen and Carbon Dioxide: The Effect on Yield of Oil Plam Kernel Shell. Procedia Chemistry. 2014; 9:194–201. Crossref
- Bach Q-V, Tran K-Q. Wet Torrefaction of forest Residues-Combustion Kinetics. Energy Procedia. 2015; 75:168–73. Crossref
- 12. Eseltine D, Thanapal SS, Annamalai K, Ranjan D. Torrefaction of woody biomass (Juniper and Mesquite) using inert and non-inert gases. Fuel. 2013; 113:379–68. Crossref
- Couhert C, Salvador S, Commandre JM. Impact of torrefaction of syngas production from wood. Fuel. 2009; 2286–90. Crossref
- 14. Uemura Y, Omar W, Tsutsui T, Yusup S. Torrefaction of oil palm wastes. Fuel. 2011; 2585–91. Crossref
- 15. FluidChe. 2017. Available from: http://fluidsche.ump.edu. my/index.php/en/
- 16. The Center of Excellence for Advanced Research in Fluid Flow (CARIFF). Available from:http://cariff.ump.edu.my/
- Natural resources products prospects International Conference on Fluids and Chemical Engineering FluidsChE 2017 Malaysia, Special Issue 2, Vol: 1. Indian Journal of science and technology. 2017 10 (16) DoI: 10.17485/ijst/2017/ v10i16/111938
- 18. University Malaysia Pahang. www.ump.edu.my