Slow pyrolysis of Durio zibethinus rind and the influence of carbonization temperature on biochar properties

A Selvarajoo
Department of Chemical and Environmental Engineering, Faculty of Science and Engineering, University of Nottingham Malaysia, Jalan Broga, 43500 Semenyih, Selangor, Malaysia
Anurita.Selvarajoo@nottingham.edu.my

Abstract. Due to rapid development in some countries that puts increasing urgency on the global community to replace non-renewable resources, Interest in harnessing energy from other sources like biomass has grown immensely in recent years. Pyrolysis is one the thermo-chemical methods to transform biomass into useable fuels. Pyrolysis conducted without the presence of oxygen at high temperatures results in the production of biochar, bio-oil and gases. The aim of this work was to perform pyrolysis experiments for durian rinds with the emphasis on the characterization of the rinds and their biochars. The pyrolysis of durian rinds was performed in a horizontal tubular reactor at temperatures ranging from 300 to 700 °C. The effects of temperature together with holding time on the yield of biochar, heating value and elemental composition of the biochar were investigated. It was found that the pyrolysis operating temperature had a significant effect on the yield of biochar, heating value and elemental composition of the biochar. Increment of pyrolysis temperature from 300 to 700 °C, showed a decrease in the total biochar yield, while the heating value increased. The optimum temperature was found at 325 °C with a holding time of two hours. The biochar yield obtained at optimum temperature was 40.8 %wt with a heating value of 28.7 MJ/kg. In conclusion, the results from the pyrolysis showed the durian rinds has potential to be converted into solid biofuel that can be used for energy application.

1. Introduction
Due to the growing realisation that biomass wastes are valuable feedstocks, ways have been identified to utilise them. A few thermal conversion methods have been applied to biomass for its utilisation. Some of which includes the traditional process of direct combustion where the biomass is burnt in the presence of air to obtain heat or electricity [1]. Other processes include biomass gasification and biomass liquefaction. Biomass gasification is a process where the biomass’ lignocelluloses materials are left to react with gasifying agents like CO2 to generate gas mixture which is combustible. Liquefaction of biomass however utilizes the waste by converting it into liquid hydrocarbon mixture that usually generates solid residues and gaseous by-products [1]. Pyrolysis has been widely researched in current times due to its efficient thermal conversion and green technology [2]. Pyrolysis of biomass includes heating the biomass in an oxygen-free environment up to 1500°C. The long chains of biomass that contain carbon, hydrogen and oxygen compounds will be broken down into three types of fuel products namely syngas, bio-oil and biochar. Generally, pyrolysis can be categorized into slow pyrolysis, fast pyrolysis and flash pyrolysis [1]. Usually the product composition changes depending on the type of pyrolysis.
The solid product obtained from the biomass pyrolysis process is called biochar. Due to its high carbon content and high porosity, biochar can be applied in a wide range of applications. Biochar can be utilized as an alternative energy source to replace the current heavy dependency on fossil fuels. Biochar is also used as a low-cost metal adsorbent for soils and its porosity facilitates infiltration of percolating groundwater [3]. To get high yields of biochar product from biomass wastes, slow pyrolysis is preferred where moisture and volatile compounds will be released from the biomass, leaving the porous structure retaining aromatic compounds and chemical functional groups of the biochar [4]. Current developments and research have investigated on biochar that are derived from fruit wastes like banana peels [1], mango endocarps [5], rambutan peels [6], oranges [5] and many more. All these wastes are abundant in supply in Malaysia. However, the use of durian rind as a feedstock for pyrolysis for biochar production is less studied in Malaysia.

Durian (Durio zibethinus Murr.) is a tropical fruit native in Southeast Asia. Due to its unique flavour and taste, durian became one of the prominent fruits for Southeast Asians [7]. The average size of durian is in between 2 and 4.5 kg [8]. The edible part of the fruit accounts only 15-30% of the weight of the entire fruit. Thailand and Malaysia are the primary producers of durian. Production of durian in Malaysia reached 384,170 tonnes per year in 2018 with a planted area of 72, 536ha [9]. Durian rind generated approximately 21, 200 tonnes. Durian season in Malaysia begins in June and extends through August. During the season of durian, a massive amount of the rind is disposed as wastes. Excess agricultural waste during this season is anticipated to increase in the future and could lead to environmental problems.

In this study, durian rinds were selected as feedstock for pyrolysis process to produce biochar. Optimum operating pyrolysis conditions: operating temperature and holding time were determined to produce biochar. The feedstock and the respective biochar was characterized through proximate analysis, ultimate analysis and heating value determination.

2. Material and Method

Air-dried durian rinds were ground in a Retsch grinder. Then, the samples were sieved to obtain a homogenized samples with size of 1-2mm. 20 g of the sample was fed into the pyrolysis tubular reactor (Carbolite model STF 12/65/550) for each pyrolysis run. The pyrolysis tubular reactor has an inner stainless steel working tube with a dimension of 50 mm inner diameter and 1200 mm length. The schematic diagram of the experimental setup is shown in Figure 1. Before the start of the pyrolysis experiment, the sample will be purged with nitrogen gas to completely remove the presence of oxygen. Then, the pyrolysis experiment is performed at 300 °C at a heating rate of 5 °C/min and holding time of 3 hours. The experiment is repeated for different operating temperature of 500 and 700 °C and different holding time of 0 to 3 hours. After each test, the resulting biochar was collected and weighed. The yield was calculated using Equation (1).

$$Biochar \ yield \ (%) = \frac{m_1}{m_2} \times 100$$

where:

- $m_1$ is the weight of biochar in grams;
- $m_2$ is weight of sample in grams;
Figure 1. Experimental setup for the pyrolysis

Proximate analysis is the determination of moisture content, volatile matter, fixed carbon and ash content of a sample. For this study, the proximate analysis for the durian rind and its respective biochars was carried out using Thermo-Gravimetric Analyzer (TGA/DSC1 Stare System Mettler Toledo). Ultimate analysis is the determination of elemental composition (C, H, N and S) of a sample. Ultimate analysis, was determined using an elemental analyzer (ThermoFinnigan Model Eager 300 for EA1112). Bomb calorimeter (Model 6100 Parr Instruments) was used to carry out the heating value determination of the samples. The thermogravimetric (TG) analysis of the durian rind sample was carried out in a Thermo-Gravimetric Analyzer (TGA/DSC1 Stare System Mettler Toledo). For the TG analysis, 50 mg of the sample was loaded into TGA. The sample was heated from room temperature to a temperature of 110 °C at 5 °C/min. The weight loss at this point is taken as moisture content. Then, the sample is heated to 920 °C at a heating rate of 5 °C/min. The weight loss at this point is taken as volatile matter content. After that, the sample was cooled down to 825 °C and switched to oxygen flow to allow combustion process to take place. The weight remaining after combustion process is taken as ash content. Fixed carbon is then calculated using Equation 2. From the TGA, the continuous records of weight loss and temperature can be obtained. This can be used to also predict the biochar yield and to determine rate of degradation of sample.

\[ \text{Fixed carbon (\% wt)} = 100 - \text{Moisture content} - \text{Volatile matter content} - \text{Ash content} \]  

3. Results and Discussion

3.1 Durian Rind Pyrolysis

Heating value of the durian rind pellets was 14.9 MJ/kg, which was lower than the calorific value of and olive husk (19.0 MJ/kg) but similar to rape (15.3 MJ/kg) and sunflower (15.7 MJ/kg) [10]. Table 1 summarizes the composition of air-dried durian rind obtained from proximate and ultimate analysis. Durian rind has a low ash content and a high volatile matter content. Durian rind is an oxygen and carbon rich feedstock but has hydrogen content.

| Analysis             | Ref. [11] | Ref. [12] | This study |
|----------------------|-----------|-----------|------------|
| Proximate (wt%)      |           |           |            |
| Moisture             | 5.53      | 2.95      | 8.69       |
| Volatile Matter ^a   | 69.59     | 72.56     | 82.47      |
| Ash                  | 2.52      | 5.67      | 3.08       |
| Fixed carbon ^a      | 22.36     | 18.82     | 5.76       |

[^a]: All values are in wt%.
Ultimate (wt (%))

|       |         |         |         |
|-------|---------|---------|---------|
| Carbon| 60.31   | 43.91   | 40.47   |
| Nitrogen| 3.06   | 1.47    | 0.82    |
| Hydrogen| 8.47   | 5.87    | 5.47    |
| Oxygen | 28.06   | 40.03   | 53.24   |

*Calculated by difference

Before pyrolysis, durian rind cannot be regarded as valuable fuel. Comparing the heating value and carbon content of coal, durian rind has much lower values. But the durian rinds can be upgraded to biochar, a solid that would benefit greatly from upgrading. Figure 2 depicts the biochar yield and heating value for carbonization of durian rind at different temperature. The experiment was carried out at a heating rate of 5 °C/min to temperature setting of 300, 500 and 700 °C and dwelling time of three hours at the set temperature. As can be seen, temperature has significance effect on the biochar yield. With increasing carbonization temperature, the yield of biochar decreased. When the temperature was raised from 300 to 700 °C, the biochar yield decreased from 50.5 to 27.6%. Heating value of the biochar increased with the temperature from 14.9 to 25.6 MJ/kg. From the results, optimum temperature to obtain high yield of biochar (39.6%wt) with heating value of 29.75 MJ/kg was at 325 °C. Biochar yield and heating value in between 0 to 3 hours was investigated to determine the optimum holding time. This is an important parameter as longer holding time will lead to an increase in the total energy consumption during the pyrolysis process. Figure 3 shows the effect of holding time on the biochar yield and heating value of the biochar. From the results obtained, it showed that when the holding time increased, the biochar yield decreased. The reason behind this maybe because the sample did not reach the dwelling temperature when the furnace reached the set temperature. There was a temperature lag between the furnace and the sample temperature. However, incomplete carbonisation might have occurred at the earlier stage of the holding time that results in higher biochar yield with lower heating value. Thus, dwelling time of two hours suffices to obtain a reasonable biochar yield of 40.8% and heating value of 28.7 MJ/kg. Results by Apaydın-Varol et al. showed that a maximum biochar yield of 28% was obtained at 300 °C for pistachio shell pyrolysis experiments [13]. Demirbas reported biochar yield of around 44%, 38% and 30% were obtained for olive husk, tea waste and corn cob respectively at temperature of 550K [14].

**Figure 2.** Effect of pyrolysis temperature on biochar yield and heating value
3.2 Analysis of durian rind biochar
With increasing temperature, carbon content of the biochar increased. When the final temperature was increased from 300 to 700 °C, the carbon content increased from 40.47 to 67.67%. Decrease of hydrogen and oxygen content was also noticed when the operating temperature increased. The content of hydrogen decreased from 5.47 to 1.39% while oxygen decreased from 53.24 to 29.70%. Low oxygen content is one of reason that explains a higher heating value of the biochar [15]. Figure 4 shows the elemental composition of durian rind versus heating value. As can be seen from Figure 4, heating value increased with increasing carbon. Similar trend noticed for (carbon + hydrogen) contents of the sample. Table 3 shows the elemental composition and the heating value obtained for biochar at optimum carbonization temperature, 325 °C.

![Figure 3. Effect of holding time on biochar yield and heating value](image)

![Figure 4. Plots of element contents of durian rind vs heating value](image)
Table 2. Elemental composition and heating value of durian rind optimum biochar

|       | C   | H   | N   | O   | GHVb |
|-------|-----|-----|-----|-----|------|
| Biochar | 54.83 | 4.83 | 0.99 | 39.34 | 28.7 |

a Calculated by difference

b Gross heating value (MJkg⁻¹)

3.3 Thermogravimetric analysis of durian rind thermal conversion

Thermogravimetric behaviour of the durian rind at heating rate of 5 °C/min is shown in Figure 5. The rate of loss in mass versus temperature, derivative thermogravimetric (DTG) profile is shown in Figure 6. The DTG curve was derived from the TGA curve. The first stage of the weight loss occurred when the sample is heated from room temperature to a temperature of around 110 °C. Weight loss at this stage corresponds to the loss of water in the biomass sample. At the second stage, there was one observable peak in between 240 °C and 350 °C in the derivative plot. As suggested by Chandra et al. [16], it corresponds to the volatile matter released from the sample. The mass loss rate of biochar was 1.44 mg/min at 300 °C, the highest peak reached. At temperature above 350 °C, some structure decomposition within the sample still takes place. Due to this there was continuous weight loss from 350 to 920 °C. Total weight loss at this stage for durian rind was 86.21%. The TGA plot of durian rind was similar to the plots of González et al. [17] but the ranges of temperatures and the rate of mass loss were different. In the active zone, the main decomposition of hemicellulose together with cellulose attributed to the release of volatile compounds. In the passive zone, lignin and cellulose decomposition occurred contributing to high volatile compounds released [17]. These two distinct pyrolysis zones were observed in Figure 6. The first zone is the active pyrolysis zone where up to temperature of 300-350 °C, there was sharp increase in the mass loss rate of the samples. The second zone is passive pyrolysis zone where a slow further loss of weight observed up to temperature of around 600 °C. However, at temperature above 600 °C, there was slight change in the weight loss. Demirbas mentioned in his work that at temperatures of 470–530K, break down of hemicelluloses will happen first. This is followed by decomposition of cellulose in the temperature range 510–620K. Then, finally the last component to decompose is lignin at temperatures of 550–770K [14].

![Figure 5. TG curve of durian rind](image-url)
It is important to characterize durian rind feedstock and the biochar to understand their composition and determine their suitability to be used as solid fuel. From this study, durian rind was carbonized to the right extent to obtain biochar at optimum temperature and holding time. However, there are more analyzes that need to be carried out to understand the surface characteristics, surface area, porosity and obtaining the functional groups to improve the surface characteristics of biochar to be better suited for its desired application. Biochar obtained from this study could be used as a solid fuel to supply sufficient energy in boilers. Biochar could also be used as feedstock for other thermal conversion process like gasification to produce hydrogen rich gas.

4. Conclusion
Biochar can be obtained from pyrolysis process. At different pyrolysis temperature, biochar obtained are rich in carbon with high heating value. Durian rind and its respective biochar were characterised by proximate and ultimate analysis. The major parameters that influence the biochar from durian rind are temperature and holding time of the sample. Pyrolysis temperature of 325 °C and holding time of 2 hours was found to be the optimum conditions to obtain a high heating value biochar, 28.7 MJ/kg with 40.8% of biochar yield. The biochar obtained from pyrolysis can be a good feedstock for gasification.

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