Pyrolysis of Pineapple Peel

Effect of Temperature, Heating Rate and Residence Time on the Bio-char Yield

Anurita Selvarajoo and Svenja Hanson

Abstract— **The depletion of fossil fuel is creating awareness of the need for a sustainable future, and interest in alternative energy sources has increased tremendously in recent years. Pyrolysis is one of the efficient thermo-chemical method of harnessing energy from biomass. The aim of this work was to conduct an experimental study on the pyrolysis of pineapple (Ananas comosus (L.) Merr.) peel with the emphasis on the characterisation of the peels and their chars. Pineapple peel was pyrolysed in a horizontal tubular reactor under inert atmosphere. The effects of pyrolysis temperatures, heating rates and residence time on the yield of the bio-char were investigated. Pyrolysis runs were performed at temperatures between 300 and 700 ^{0}C with heating rates of 5 and 50 ^{0}C min^{-1}. The residence time was between 0 to 3 hours. The obtained bio-char ranged between 29.3 and 47.1 %wt, at different pyrolysis conditions. The optimum bio-char yield was obtained at 425 ^{0}C with a heating rate of 5 ^{0}C min^{-1} and residence time of 1 hour. According to the results obtained under the conditions of this study, the pyrolysis temperature had the most significant effect on bio-char yield compared to heating rate and residence time. The results from the pyrolysis showed the potential of pineapple peel as an important source of solid fuel.**

Keywords— **Pyrolysis, Bio-char, Biomass, Pineapple**

I. Introduction

Pineapple (*Ananas comosus* (L.) Merr.) is an important tropical and subtropical plant widely cultivated in many places including Hawaii, Philippines, Thailand, Malaysia, Mexico, South Africa and China [1]. They grow only in tropical lowlands but are relatively drought tolerant. The fruit may be oval or cylindrical and grows out of the ground surrounded by a rosette of waxy, strap-like leaves that have spines at their tips.

Malaysia is the world's 17th largest producer of pineapple and in the year 2012, the production of pineapple reached 334,400 tonnes [2]. The planted area in that particular year was 15,611 hectares. Pineapple is widely grown in the state of Johor, Selangor, Kelantan, Sarawak and Penang in Malaysia [3].

Numerous studies on pineapple wastes can be found in open literature. Mainoo et al. [4] reported that pineapple waste can be decomposed in vermicomposters by *E. eugeniae*, a native earthworm, recycling this waste into a soil amendment, a simple and low cost technology. In the biotechnology field, a

few researches reported on extraction and purification of bromelain from pineapple peels [5-7].

Hu et al. [8] prepared hydrogels and polyvinyl pyrrolidone (PVPP) composite hydrogels from pineapple peel cellulose with 1-allyl-3-methylimidazolium chloride via different heating and cooling processes. Pineapple peels which have a high content of cellulose and hemicellulose were used in the production of bioethanol by fermentation [9] and biomethane through anaerobic digestion [10]. Apart from pineapple peels, investigations on other wastes from pineapple were reported elsewhere. Pineapple leaves [11, 12] and stem [13] were utilized as low-cost adsorbent to remove basic dye (methylene blue and basic green 4) from aqueous solution by adsorption. In a different study, the juice of rotten or discarded pineapples was used for ethanol production [14]. Citric acid was derived from pineapple wastes and used in the removal of heavy metals from contaminated sewage sludge [15, 16].

In general, considerable research has been conducted in producing char using different agricultural wastes as raw material such as residues of rape and sunflower [17], almond shell, walnut shell, almond tree pruning, olive stone [18], olive husk, corncob, tea waste [19], pistachio shell [20], rice husk [21], sunflower shell, pinecone, rapeseed, cotton refuse, olive refuse [22], sugarcane bagasse [23], wood, hazel nut shells, olive husks, corn cobs, wheat straw, Lucerne pressed cake [24], and corn stover [25]. However, the use of pineapple peel as a feedstock for pyrolysis for bio-char production has never been studied. The objective of this study was to determine the optimum pyrolysis temperature, heating rate and residence time for the formation of bio-char.

II. Materials and Methods

The sample of pineapple peel was obtained from a juice processing mill in Johor, Malaysia. The freshly obtained biomass has a very high moisture content of around 82% wt. As an initial step, the samples was cut into smaller pieces to a dimension of 1 x 5 cm to increase the surface area and left for air drying. The moisture content of the samples was determined by air-drying 20 g of the sample and weighing it at time interval of 24 hours until there was no significant change in the weight. If the sample was not suitable for air-drying due to very high moisture content, which can induce mould growth, it was then oven dried at temperature of 80 ^{0}C to attain the moisture that corresponds to the air-dried moisture content. Once the air-dried moisture content was achieved, the samples were ground using a grinder (Retsch, model SM100) to a particle size of ≤5 mm. The samples were then sieved using sieves and a sieve shaker. Sieve sizes of 2 mm and 1 mm were

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used to segregate the samples. The sample fraction retained on the 1 mm sieve was used for further analysis. The fine particles that pass through the 1 mm sieve were discarded as fine particles may cause blockage to the pyrolysis unit.

The pyrolysis experiments were carried out in an electric tubular furnace, Carbolite model STF 12/65/550. The main component was the stainless steel cylindrical working tube of length 1200 mm, inner diameter 50 mm, outer diameter 60 mm inserted into electrically heated tubular furnace. A thermocouple was placed in the middle of the working tube to obtain the sample temperature. A 20 g sample of pineapple peels was placed inside the working tube of which the inlet was connected to a nitrogen (N_2) tank. The flow rate of N_2 was 2 Lmin^{-1}. The outlet of the working tube was connected to a volumetric flask with sidearm submerged into a 5 liter beaker filled with distilled water. Prior to each run, the reactor was purged with N_2. Pyrolysis was carried out at temperatures in the 300 to 700 ^{0}C range with a heating rate of 5 ^{0}Cmin^{-1}. At the end of the run, the tubular furnace was switched off and was left to cool to room temperature. The resulting bio-char was collected and weighed after each test. The yield was calculated using (1).

$$\text{Char yield (\%)} = \frac{m_1}{m_2} \times 100 \qquad (1)$$

m_1 is the mass, in grams, of the char;
m_2 is the mass, in grams, of the sample;

The thermogravimetric (TG) analysis of the pineapple peel sample was carried out in a Thermo-Gravimetric Analyzer (TGA/DSC1 Star^e System Mettler Toledo) using nitrogen and oxygen. In the TG analysis, 50 mg of the sample was loaded into the instrument and heated from room temperature to 920 ^{0}C at a heating rate of 5 ^{0}Cmin^{-1} in nitrogen flow during pyrolysis test. The continuous records of weight loss and temperature were obtained. It was used to predict char yield and to determine degradation rates. The heating value of the air dried pineapple peels and the pyrolysis char were carried out using an oxygen bomb calorimeter (Model 6100 Parr Instruments).

III.   Results and Discussions

Studies using pineapple peels for pyrolysis to produce solid fuel are scarce and this common Malaysian biomass waste has never been thoroughly explored. In this work pineapple peels was studied for determining the main characteristic of raw biomass and their respective chars, and quantify the yield of their solid pyrolysis products. The effect of temperature was investigated together with heating rates and residence time.

A.   Effect of Temperature

To determine the effect of temperature on char yield and heating value, pyrolysis experiments were conducted at temperatures ranging from 300 to 700 ^{0}C. The yield of char was calculated using (1) and the average was taken for each
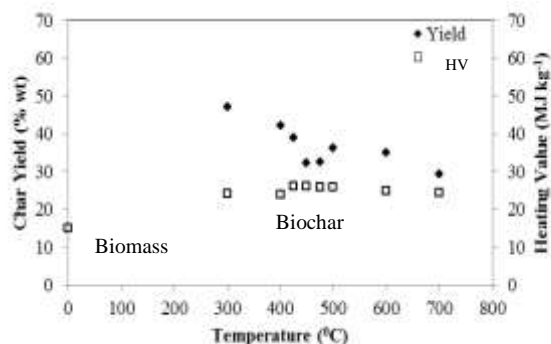

Figure 1 : Effect of temperature on char yield and heating value of biomass

corresponding temperature. The trend of char yield and heating rate at different temperature set points is shown in Fig.1. The char yield decreased with increasing pyrolysis temperature. The decrease was 46.4 % (from 47.1 to 29.3 % wt) when the temperature increased from 300 to 700 ^{0}C. Based on the results, pyrolysis runs were conducted in smaller temperature intervals to find the optimum temperature for maximum char yield with highest heating value. The samples were carbonized to the extent just to produce enough char with moderately high heating value. Optimum temperature for carbonization was at 425 ^{0}C for pineapple peels. It was recorded that the char yield at optimum temperature was 39.0 %wt. Heating value for pineapple peel char was 26.1 MJ kg^{-1}.

Thermogravimetric behaviour of the samples at heating rate 5 ^{0}Cmin^{-1} in nitrogen atmosphere is shown in Fig. 2. Derivative thermogravimetric (DTG) profiles of the samples, which show the rate of loss in mass versus temperature, were derived from the TGA curves as shown in Fig. 3. The first stage of the weight loss was observed when the sample was heated from 25 to 110 ^{0}C. Weight losses incurred were 9.9 %. It may correspond to the loss of water and light volatile compounds in the pineapple peel sample. As can be observed, devolatilization of pineapple peel started at temperature 211 ^{0}C. The weight loss started to decrease rapidly after that temperature. This corresponds to the release of volatile matter from the biomass. The DTG peaks differ in position and height.
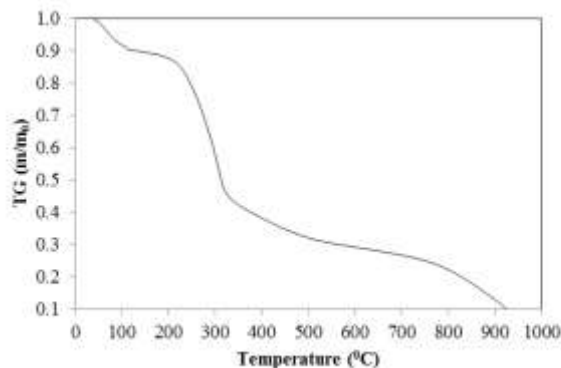

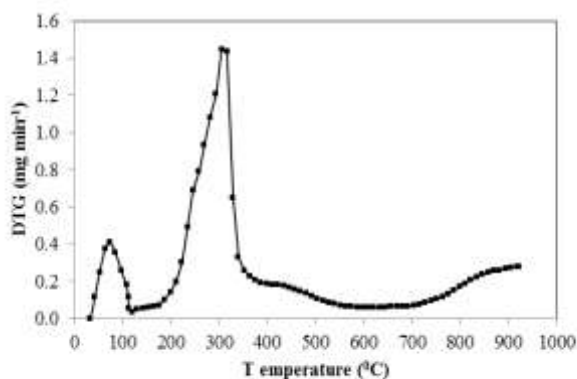Figure 2 : TG curve of different biomass sample

Figure 3 : DTG curve of different biomass sample

At the second stage, the derivative plot showed one observable peak at 305 ^{0}C. Maximum rate of weight loss at the peak temperature was found to be 1.45 mgmin^{-1}. Major devolatilization for pineapple peel ended approximately at 399 ^{0}C. Most of the weight loss occurred at this zone where pineapple peel lost 48.5 % of the total weight. This shows that almost half of the weight loss was during the devolatilization between temperatures 154 and 423 ^{0}C. Average degradation rates at this zone were 0.62 mgmin^{-1}. After this temperature slight devolatilization occurred where constant weight loss had been recorded and represented by the long tailing section. It can also be seen that the rate starts to increase slowly again at around 600 ^{0}C. The total weight loss at the end of 920 ^{0}C was 90.4 %.

From Fig. 1-3, it illustrates that with increasing operating temperature, the weight loss increased. With increasing temperature, char yield decreased as the weight loss is higher primarily due to the initial large amount of volatiles that can be easily released. To a lesser extent, the release of moisture also contributes to the weight loss. As the pyrolysis proceeded, the gas generated reduces the mass of the remaining char and also reduced the volatile matter of the biomass [26]. The reducing char yield with increasing pyrolysis temperature are in line with findings from other studies found in literature [19-21, 26-30]. However, unique trend was observed for pineapple peels in Fig.1, the char yield dropped at temperature 450 and 475 ^{0}C and increased back at carbonization temperature 500 ^{0}C. This phenomenon is not reported in any other studies in the literature. The possible cause for a drop in char yield could be due large amount of volatiles that was released during pyrolysis at temperature 450 and 475 ^{0}C. Destruction of cellulose and hemicelluloses that occur before 400 ^{0}C could have change the char surface morphology which leads to faster decomposition of the char. This is purely based on assumptions and further tests need to be conducted to explain this phenomenon. Definitely, biomass cannot be represented by a single homogeneous material and therefore, it is necessary to examine the pyrolytic products of biomass by simultaneously considering the differences in the physical texture (e.g. the distribution of hemicellulose, cellulose, lignin,

and minerals in biomass) and chemical structures (e.g. functional groups and chemical bonds) [27].

Furthermore, Demirbas [31] stated in his findings that the heating value of the char increases with increasing both heating rate (from 2 to 100 ^{0}C s^{-1}) and temperature up to 477 ^{0}C from pyrolysis of beech trunk barks. On the other hand Apaydin-Varol et al. [20] reviewed and stated that higher final temperatures (600 ^{0}C and above) favour gas formation and relatively lower temperatures (400 ^{0}C and below) favour char formation. Parihar et al. [23] also concluded a decrease in char yield with an increase in temperature and attributes it to a greater primary decomposition at higher temperature or to secondary decomposition of the char residue. During secondary decomposition, the char may also produce non-condensable products which would also contribute to the increase in gas yield with increasing temperature of pyrolysis. The effect of temperature on the biochar yield on pineapple peel are in agreement with the previously reported results in the literature for grapeseed and chestnut shell [32], hazelnut shell, walnut shell, almond shell and sunflower shell [33], grape bagasse [34] and pistachio shell [35]. For a high char production, a low temperature, low heating rate process would be chosen [19].

B. Effects of Heating Rate

Under the optimum pyrolysis temperature found for the pineapple peel, the effect of heating rate was investigated using 50 ^{0}C min^{-1} representing high heating rate. Table 1 lists the data from the heating rate experiments. Percentage yield for each sample were calculated for low and high heating rate at their corresponding optimum temperature. It can be seen that lower heating rate, 5 ^{0}Cmin^{-1} gave a higher yield of char compared to higher heating rate 50 ^{0}C min^{-1}. However, the percentage yield does not differ much. Pineapple peel showed a difference of 4.8 % in the char yield.

This finding is in line with Demirbas [31] and Chen et al. [36]. It was explained by Tran and Rai [37] that rapid heating leads to fast depolymerization of the solid material to primary volatiles, while at lower heating rates dehydration to more stable anhydrocellulose is limited, thus more yield can be obtained at lower heating rates. High heating rates favour higher liquid yields [20, 38]. Thus, it can be concluded that heating rate has an effect on the char yield, but unless very high rates are employed it is minor compared with the effect of the final carbonisation temperature considered preciously. Further studies on variations within the low heating rate bracket are not recommended, as a tenfold increase from 5 to 50 ^{0}C min^{-1} had comparatively little effect.

TABLE I.   CHAR YIELD AT DIFFERENT HEATING RATE

Sample	Heating Rate	
	5 ^{0}C min^{-1}	50 ^{0}C min^{-1}
Pineapple Peels	39.0	34.2

C. *Effects of Residence Time*

Optimum residence time was investigated by obtaining char yield and its heating value at smaller time intervals between 0 to 3 hours for the pineapple peel samples. This factor was taken into account as longer residence time will undoubtedly increase the total energy consumption for the pyrolysis process. Variation of char yield and heating value with residence time for pineapple peel are plotted in Fig. 4. For pineapple peels, the char yield and heating value does not show much variation as the residence time increased.

However, the energy content in the char was determined assuming 1 kg of sample carbonised at the optimum temperature. The results are plotted in Fig. 4. Although no residence time was required to obtain char with highest energy content, it cannot be justified as the sample temperature lagged from the furnace temperature and needed sufficient time to reach and stabilize at the operating temperature. Energy content of pineapple peels was 9.2 MJ at holding time of 30 minutes and increased to 10.2 MJ at 60 minutes and remained the same energy content for longer holding time. Thus, optimum residence time with highest energy content was chosen. Optimum residence time pineapple peels was 1 hour. It shows that the biomass samples did not need residence time of 3 hours to complete pyrolysis which eventually increase the cost of operation.
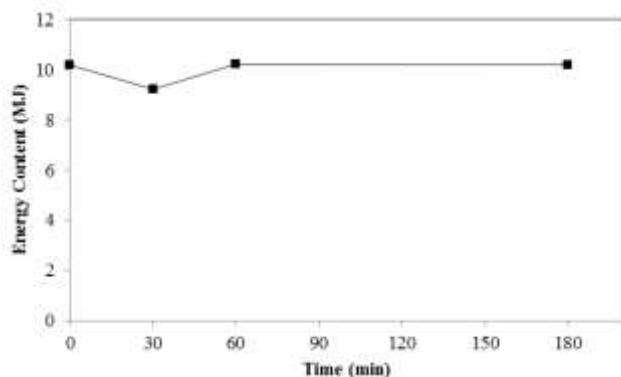

Figure 4: Energy content of char at different residence time

IV. **Conclusions**

Pineapple peel was studied for determining the main characteristic of raw biomass and their respective char and to quantify the solid product. The effect of temperature was investigated together with heating rate and residence time. The purpose of this study was to determine the characteristics of raw biomass and their char formed for their applicability as solid fuel. Process parameters were optimized to establish biochar as a potential solid fuel. Along with the previously described findings, this illustrates that temperature is the most important factor determining the char yield The optimum condition for pineapple peel was at 425 ^{0}C with a heating rate of 5 ^{0}C min^{-1} and residence time of 1 hour with char yield of 37.6 % wt and heating value of 27.2 MJ kg^{-1}.

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