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Properties of Malaysia Bamboo's (Gigantochloa Scortechinii) Pyrolyzed Products via Drop Type Pyrolyzer Reactor: Bio-Oil

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In line with Malaysia direction toward clean and sustainable renewable energy, this paper investigates the feasibility of bamboo species as a bio-energy feedstock in Malaysia as it is one of the fastest growing plants in the world. This paper will present fuel properties of bamboo species viz. *Gigantochloa scortechinii* upon fast pyrolysis technique. Three temperatures 450, 500 and 550 °C by drop type reactor with particle size in the range of 250-500 μm were investigated. Yield of bio-products was determined as well as basic chemical and fuel properties of bio-oil, -char, and -gas. Among these three temperatures, the predominant temperature with highest bio-oil at 450 °C, char at 450 °C, and gas at 550 °C were obtained indicating optimal reaction temperature. The main compounds of their bio-products are acids, phenols, ketones, and furans compound class. Advantageous determined was better quality of bamboo pyrolysis-oil was produced as it raw bamboo, bio-oil, and –char contained relatively low content of nitrogen and sulfur components.

1. Introduction

Malaysia is well endowed with renewable energy biomass resources and the widely availability of these resources (soil and water base plants to waste products) are expected to be the backup energy as well as clean energy to the so called petroleum-derived energy. Hence, the natural and plantation forest species are considered as main candidate to be a potential feedstock (Anon, 2013). Among all forest crops, bamboo has always been chosen for experimented because of the vast population, highly renewable course, its variety, and as eco-friendly species. China the world top five biomass power capacity producers has identified herbaceous (bamboo) plants as potential biofuel feedstock. As Malaysia has more than 70 species of bamboo, 25 of which are indigenous while the rest are exotics (Wong, 1989) it has considered bamboo as potential feedstock for bio-fuel production and to break it traditional application. Among bamboo species, *Gigantochloa scortechinii* species has been given considerable attention for its larger size (diameter of 6.5 cm and grows up to 14 cm) and it has the highest relative density of 58.8 % compared to other species (e.g. species grows in Kuala Keniam Forest, Pahang) (Asari and Suratman, 2011). Moreover, the rate of growth is also fast with average maturity age of 2-3 y and therefore it could supply biomass (the culm part) of 6.88 Mt/y (metric). Bamboo has been planted in Malaysia for multiple purposes with on average the export of bamboo products for a period of 10 y was only RM 250,000 as reported in (Maskayu, 2013) and in particular *G. scortechinii* was commonly used for construction. Despite its wide application for the wood-industry products, there is not much has been done to utilize bamboo for the biofuel products. Few papers reported on bamboo pyrolysis unfortunately non from Malaysia bamboo species (Lou et al. 2013; Kantarelis et al. 2010). Thus, the aim of this experiment is to investigate feasibility of utilizing bamboo as bio-energy feedstock. In this study, the bamboo was pyrolyzed in a drop type pyrolyzer. This is a simple fast pyrolysis system applying drop biomass way. The bio-products properties of fuel related components were obtained by decomposition of bamboo at three temperature, 450, 500 and 550 °C. Analysis of the bio-oil product was the focal point of interest for this paper, however,

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analysis of bio-char and bio-gas were also conducted. Hence, the objectives of this study are; to assess the biofuel related properties of bio-products from different temperatures by drop type reactor and to investigate the relationship between different temperature and properties of bio-products produced. The outcome of this study shall be the guidance on the feasibility of Gigantochloa bamboo usage and will be the basis for comparative study of bamboo species selection for bio-energy sector.

2. Material and Methods

2.1 Sampel Preparation

Samples of *Gigantochloa scortechinii* was harvested from Tasik Banding Gerik, Perak Darul Ridzuan (estimated age was over 3 years) and it culm was used for this study. The bottom and top of the bamboo was removed prior to cutting into 1 m length. These culms were washed for any contamination and debris (such as fungi or sand). The bamboos obtained have culm size 15 cm diameter and 80 cm height. Then woody stem of bamboo was further cut to small size, approximately 7cm × 1cm × 1 cm (Figure 1). The samples were further dry in an open air to dry the surface of bamboo (air dry) for overnight and oven at 105 °C for 24 h to get less than 10 % moisture (approximately 5 %). The dry samples were ground into homogeneous particle to pass through 250 μm (low speed granulator to reduce size from flake to less than 4 mm; mill pulverizer to produce powder of 250 μm). Then, samples were stored in air-tight container for next step pyrolyze and analyses.

Figure 1. Bamboo; raw, open air drying and grinded samples (200-500 μm) (left to right)

2.2 Pyrolysis Setup

Pyrolysis of 15 g bamboo sample was conducted in a bench-scale drop type pyrolyzer. Three different temperatures were applied, 450, 500 and 550 °C. As shown in Figure 3, the reactor consisted of electrical heater and insulation as the reaction may reach up to 600 °C. It has cylindrical shape and was made of stainless steel. The nitrogen (inert gas) and vacuum lines were used to replace air inside the system. K-type of thermocouple is a device to measure the temperature. Once the temperature reaches desired point, the biomass was dropped into the pyrolysis zone. And, the decomposition was allowed to take place until no more smoke can be detected at the outlet of the pyrolysis zone (approximately 10 min) and no gas pulse detected is recorded. Upon reaction, three types of products were collected, char was collected inside the reactor, oil of condensed vapor in ice-traps, and gas from a teflon sampling gas bag. The obtained bio-oil products are depicted in Figure 2.

2.3 Bio-products Analyses

2.3.1. Proximate Analysis

Moisture content values based on the total weight basis moisture of original bamboo samples were determined using the oven drying method slightly modified described by ASTM D 4442 (ASTM 2007). The weight was recorded after placed in an oven for 24 h at 105 °C. The bamboo sample was cooled in a desiccator for 30 mins to avoid reintake of moisture. The sample weight was taken again for the second time and recorded. The sample was weighed interval until the decrease of weight become negligible.

Ash content analysis is done according to ASTM E1755-95 using 4 g of bamboo sample in a ceramic crucible to measure approximately the mineral content and other inorganic matter (ASTM 2003). The pre-weighed sample was combusted in a muffle furnace at 700 °C for 3 h with a heating rate 10°C/min. Fixed carbon content is calculated according to ASTM D3172-89 (ASTM 2002). Volatile matter content determination follows standard EN 15148 with slight adjustment. Weigh 2 gram±0.1 of bamboo sample into the crucible (EN 2009). Transfer the crucible into the pre-heated furnace of 900 °C for 7 minutes±5s. When cool, the weight of the crucible was recorded.

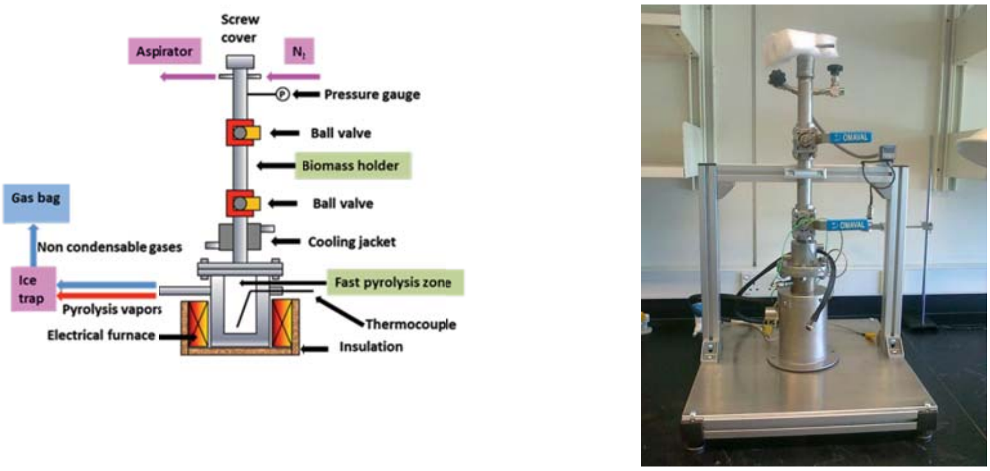

Figure 2. Schematic diagram of the drop type pyrolyzer reactor

2.3.2 Elemental analysis

The CHNS mode is used to simultaneously determine carbon, hydrogen, nitrogen and sulfur in the bamboo material. Perkin Elmer CHNS/O analyzer model 2400 was applying combustion process to break down substances into simple interested compounds. Oxygen content is assumed by the difference of 100 minus total of CHNS content by weight percentage.

2.3.3 Physical analysis

Calorific value was determined using a bomb calorimeter model C5003 series following ASTM standard E711-87 (ASTM 1996). This CV represents the latent heat of the vapor released from the sample and therefore it's in MJ/kg unit of high heating value properties. If necessary, methanol will be added to liquid sample in particular the bio-oil sample to increase the combustibility. Bulk density of the densified particulate biomass fuels with a maximum particle volume of 16.39 cm^3 (1 in.) where the sample is filled in the cylinder as ASTM E873-82 standard method (ASTM 2013). Water content in bio-oil is determined by Metrohm 870 KF Tritino Plus. The titration reagent and titration solvent used are HYDRANAL Composite 5 (Riedel-de Haen) and Methanol Rapid, respectively.

2.3.4 Chemical Analysis

Characterization of chemical composition on pyrolysis oil was done by GC-MS of Agilent Technology 7890A. Bio-oil was injected into a HP5 fused silica (5% phenyl polysilphenylenesiloxane; capillary column BPX5 with 30 m, 0.25 mm, and 0.25 μm) of its length, internal diameter, and film thickness, respectively. Oven was heated at 35 °C for 2 min prior to actual temperature 250 °C by increasing at 20 °C/mins and this temperature was held for 20 mins. Both injector and detector were set at 280 °C and the purified helium (99.999 %) was used at a flow rate of 1.5ml/min as a carrier gas.

3. Results and Discussion

3.1 Bamboo feedstock characterization

Table 1 summarized the chemical, physical and heating value properties of the Gigantochloa scortechinii bamboo used for this study. The moisture content of the samples as received (raw) and pre-dried were 41.03 and 7.33 % respectively (according to ASTM of sample preparation). In comparison, Wahab et al. (2012) determined high moisture content for this species (109.18 %) among its own genera (G. brang, G. levis, and G. wrayi) of green condition and Phyllostachys species raw bamboo as received ranged from 8-23 % (Scurlock et al. 2000). Meanwhile for pre-dried sample, this result was in the ranged from 6.0-10 % by Bhat et al. (2011) (same bamboo species). The ash content was 1-2 % or less, these ash contents are comparable to what is found other bamboo species (Hamid et al. 2012). Volatile content 72.83 % although within the range of reported by Scurlock et al. (2000) and Wongsiriamnuay et al. (2013) nonetheless they reported different bamboo species and later species not given. Fixed carbon is the remaining left which was 18.60 % and this is higher than other bamboo reported by previous authors mentioned. Heating value was found to be 16.86 MJ/kg (dry basis) and bamboo showed higher heating value than rice straw and most grasses (Lou et al. 2013; Montano et al. 2012). Carbon, hydrogen and oxygen contents were all close to literatures 46.34, 7.00 and 37.40 % respectively. From the ultimate analyses tabulated, the empirical chemical formula of G. scortechinii bamboo can be written as $CH_{1.81}N_{0.01}O_{0.60}$. Lower N and S contents are considered advantage for this bamboo species (minimal NOx and sulfur oxide conversion) as also recorded by Scurlock et al. (2000). Comparison of this bamboo species with other bamboos and bioenergy crops showed that the fuel properties are comparable and better in term of moisture, ash, gross heating value, and sulfur contents.

Table 1. Characteristic of the bamboo feedstock

Proximate Analysis	(wt%, db)	Ultimate Analysis	(wt%, db)
Moisture (as received)	41.03	C	46.34
Moisture (as pre-dried)	7.33	H	7.00
Volatile matter (as received)	42.56	N	0.55
Volatile matter (as pre-dried)	72.83	S	0.14
Fixed carbon	18.60	*O	37.40
Ash (as received)	2.03	O/C	0.60
Ash (as pre-dried)	1.24	H/C	1.81
		C/O	1.65
Empirical formula	$CH_{1.81}N_{0.01}O_{0.60}$	H/O	2.99
Calorific value, HHV (MJ/kg)		16.86	
Bulk density, (g/m^3)		0.2964	

*O is by difference, using C, H, N, S, ash, and moisture content; db, dry basis; mean values

3.2 Product Yield

The bio-product yield contents based on mass balance from pyrolysis by three different temperatures are shown in Fig 3. Besides this study on product yield, Lou et al. (2013) and Xiao et al. (2007) have been found to report on pyrolysis bamboo species however with addition of catalyst. Our liquid yields were 25.79, 24.52, and 24.38 % of 450, 500, and 550 °C respectively where it was clear that the yield was decreasing as temperature increasing and temperature at 450 °C generated the highest oil from this species. However comparing with mentioned literatures, the highest oil was obtained at 500 °C and the trend was opposite as an increase is observed with increasing temperature within the range of 400-550 °C. Gaseous product yield is increased with increasing pyrolysis temperature from 37.45 to 48.7 % following secondary cracking as secondary reaction intensified causing decreasing of liquid yield and in good agreement with these and pyrolysis of grasses and woody biomass literatures. Interestingly, char yield has lower impact from temperature as it showed that decrement is quite steady and in the range of 3%. While Lou et al. and Qi et al. reported increase and decrease yield of char product with no clear trend, Kantarelis et al. (2010) showed decrease of char yield as temperature increase. The presented yield obviously showed that no correlation between temperature and liquid yield of sample was apparent. In addition, proportional equation could be established with higher carbon and lower ash content of this bamboo will generate substantial amount of liquid yield as conversion better conversion of biofuel.

3.3 Effect of temperature on bio-products properties

In term of CV, the *G. scortechinii* bio-oil at 450-500 °C showed no different values (15 MJ/kg), this inevitably showed no impact of temperature on CV value. This value was slightly lower than raw bamboo obtained in this study (15-16 MJ/kg) and literatures (Montano et al. 2012; Jung et al. 2008). It probably attributed to the mixing of bio-oil light and heavy (upper and lower phases, respectively) that contributed to the low CV value. In opposite, it was predicted that upper phase bio-oil could reach as high as 30 MJ/kg as reported by Kantarelis et al. (2010). Note that, calorific value has no significant impact by temperature as support by liquid yield. High heating values determined proved that this bamboo is comparable to most herbaceous, agriculture and woody residues biomass (Nakagawa et al. 2007). Water content was decreased at 500 °C (64.15 %) in bio-oil from 450 °C (62.08 %) and gain water at 550 °C (69.3 %). Therefore, it could be suspected that high liquid yield at low temperature be substantially water. Nonetheless, the trivial different between the water amount of 450 and 500 °C could be considered negligible. The derived liquid from the bamboo pyrolysis at different temperature is dark and light brown in colour with two phases. The dark color looks more viscous than light brown in liquefies form. Ultimate properties are tabulated in Table 2 for bio-oil two phases and char bio-products as a function of temperature. The pyrolysis temperature had shown to have a moderate impact on these properties.

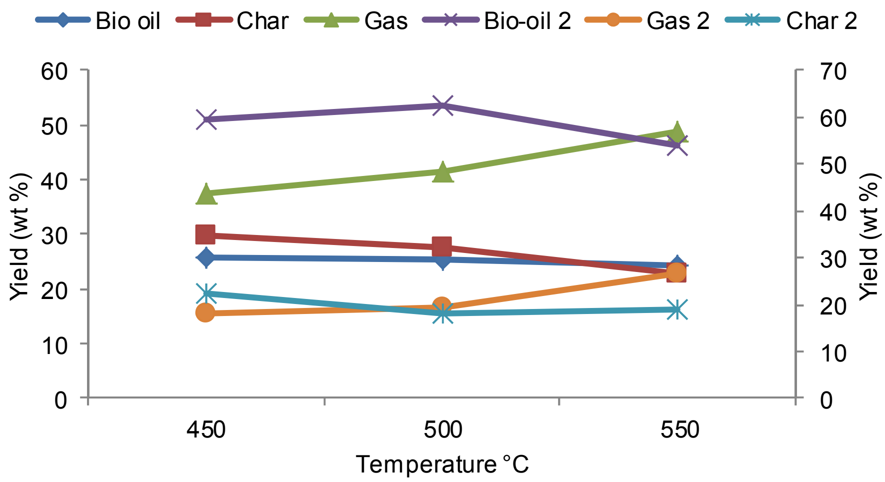

Figure 3. Bio-products yield of pyrolyzed bamboo at different temperatures – Bio-oil2, Gas2 and Char2 are from (Lou et al. 2013)

Table 2 Elemental and physical analysis of pyrolysis bio-oil

Product	*Temp*	*Elemental Analysis*					*Physical Analysis*	
		Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen [a]	CV (MJ/kg)	Water (wt%)
BioOil (light)	450 °C	20.62	7.54	0	0.01	71.83	8.76	64.15
	500 °C	23.42	9.93	0	0	66.65	9.82	62.08
	550 °C	21.05	9.44	0.04	0.37	69.1	8.41	69.3
BioOil (heavy)	450 °C	62.03	7.52	0.32	0.3	29.9	15.47	
	500 °C	53.92	7.61	0.14	0.25	38.09	16	
	550 °C	60.56	7.52	0.23	0.24	31.45	15.36	

[a] By difference; mean values

The detected components of ultimate analysis (wt %, db) of bio-oil light (upper phase) and heavy (lower phase), and also char were C, H_2, N_2, S and O_2 they have difference concentration dictated by the temperature. Carbon content was shown highest at low temperature (450 °C) in the bio-oil (heavy) which supported by Jung et al. 2008 and reduction of C content in bio-oil (heavy) resulted to it increase in light phase as can be seen at 500 °C. This could be explained by the fact that secondary decomposition of solid residue nonetheless as temperature rising to 550 °C Carbon content also rose. Apparently, correlation can be drawn between C content and temperature as well as liquid yield obtained at low temperature. Contrary to hydrogen content (H) for bio-oil (heavy) product, H did not change much and as temperature increases H increment stop at 500 °C then decrease at high temperature (550 °C) as more volatile matter converted to fuel. Meanwhile Nitrogen (N_2) and S contents could be considered negligible. Note that oxygen content are high for all temperature in the bio-oil light (upper phase) which indicate that this product require further treatment in order to be used in the energy sector. Nonetheless, this showed similar trend as reported in literatures. The characteristic of char were also examined for it ultimate analysis. Char has high C content with the elevated temperature however this value is lower than (Kantarelis et al. 2010) (536 °C) and reversely the O_2 level declined. Other components (H_2, N_2) did not showed substantial amount and sulfur content could be considered negligible.

4. Conclusions

In this paper *G. scortechinii* bamboo were pyrolyzed at three temperatures (450, 500, and 550 °C) using drop type reactor and their bio-oil was investigated. Experimental results showed that temperature dictated the bio-oil product properties. CHNS components in the bio-oil showed an impact of temperature to the desire value as carbon production is preferable and at between 450-550 °C carbon content was obtained at 60 wt% in bio-oil (heavy phase). In reverse, O_2 content become lower at high temperature for bio-oil product. Nitrogen and sulfur contents for both raw and bio-oil were considered relatively low and this is extra benefit over coal. The results proved that this bamboo species can be a new source of bio-energy feedstock.

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