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Pyrolignous Acid Production from Palm Kernel Shell Biomass

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ABSTRACT

Palm kernel shell biomass from five different oil palm mills were measured for general characteristics (ultimate, proximate and compositional analysis). The palm kernel shell with the pre-eminent result was used as a raw material to carry out pyrolysis at different temperature ranges (419 ^{o}C, 429^{o}C, 439^{o}C and 529^{o}C). The relationship between the temperature, yields and chemical composition were analysed. The pyroligneous acid with the highest yield was further analysed for physiochemical properties from the aqueous fraction extracted after storing for a month. The pyrolytic product was recommended for further studies.

KEYWORDS: Pyrolgneous Acid, Palm Kernel Shell, Biomass, Pyrolysis.

INTRODUCTION

Biomass waste management is one of the major problems arising as an effect of oil palm plantation activities. Malaysia is one of the major exporters of palm oil in the world, producing about 43.1% of the world's palm oil [10]. Thus the high quantity of biomass, palm kernel biomass can be utilized in solving environmental and economic concerns of greenhouse gases resulting from fossil fuel related activities of humans. By providing sustainable ways of managing the biomass waste, pyrolysis is one of the techniques that can be utilized in managing agricultural biomass of palm kernel shell. Pyrolysis is one of the simplest and oldest process of utilization of biomass. It is a thermochemical process (around 400-600 ^{0}C), resulting in thermal degradation of organic matter at an ambient pressure that occurs in the absence or near of oxygen [2-3]. The composition of the biomass (cellulose, lignin and hemicellulose) and operational parameters (final temperature, heating rate and residence time) affect the final composition of the products (content and the characteristic). These two factors interact during thermal degradation of biomass [11, 8].

Slow pyrolysis is characterized with slow biomass heating rates, low temperature and long duration for producing gases and solids, while fast pyrolysis takes place within five seconds at temperatures between 300-500^{0}C [4]. Slow pyrolysis provides a more useful and valuable energy products of the converted biomass, presently a lot of interest is focused on the liquid product of pyrolysis. The Pyrolytic liquid may be stored and is easily transportable to other sites. The liquid product may be utilized in heat and energy generation or may contain chemicals in economical recoverable concentrations.

Palm kernel shells (PKS) are the fractions that are left in the oil palm mills after extraction of the oil palm from the mesocarp. The nuts are broken and the kernel is removed. The hard stony endocarp covering is the PKS, which are left as the fibrous shell waste materials [12, 1]. Palm kernel shell can be applied in various fields. The managed waste products reduce environmental pollution and the effect of greenhouse gases is reduced, as a result of substitution of the biomass carbon rather than use of fossil fuels. Products of pyrolysis have various uses. Pyroligneous acid has been used for ages as sterilizing agent, deodorizer, fertilizer and antimicrobial agent and it also exhibits antioxidant activity [9].

METHODOLOGY

Sample Collection

Palm kernel shell (PKS) were collected from five different oil palm mills in Johor Malaysia which included Simpang Wa Ha, Lok Heng**,** Adela, Semenchu and Air Hitam of Felda Groups with sampling cellophane bags and labelled.

Sample Preparation

The samples received were broken in form and size of about 1-2 cm, dried and washed thrice to remove impurities and foreign substances. The samples air-dried for one week at ambient temperature of about 30^{o}C.The PKS samples crushed and grinded using a grinder to a particle size of about 450um, and passed through a sieve 40um.

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Methods

The experiments are divided into two parts. The first part include the determination of the chemical properties of the PKS biomass analysed based on component constituent (cellulose, hemicelluloses and lignin), ultimate (C, H, N, O/S elements) and proximate (moisture, ash, volatile and fixed carbon) values according to ASTM standard. The second part was carried out to determine the effect of pyrolysis temperature on pyrolysis yields. The terminal pyrolysis temperature once attained was maintained for one hour. The terminal temperature range investigated was from 419^0C to 529^0C, increasing in steps of 10^oC and different temperature ranges were utilized. Previous research by [7] indicated that pyrolytic liquid yield was highest at temperatures from 450 to 500^0C. Also, the lignin content of biomass degraded slower over temperature range of 200-500^oC. Then, cellulose and hemicellulose content thus the reason for temperature choice, the effect of the residence time at two different ranges was also compared. During the pyrolysis process, the emissions were collected in a flaska 500ml round bottom flask with clear single neck, S. T joint of 29/32 through an outlet port connected to two water-cooled condensers. The condensate collected in 2 ice-cooled spherical flasks which also had an outlet for gaseous products that could not be condensed, to escape to the outside of the laboratory at the early stage but were subsequently burned off to prevent air pollution.

Analysis

Investigation of the chemical properties of the palm kernel shell were based on standard methods. The ultimate analysis was conducted according to the ASTM E 777, E778. The proximate analysis carried out according to the ASTM standard test methods E-871, D1102, E-830, E872 and E-897.The component analysis carried out in accordance with the ASTM D1103-80 and D1104-56.

Preparation and Refinement of the Pyroligneous Acids

Thermochemical slow pyrolysis of the chosen palm kernel shell sample based on chemical analysis evaluation of the five samples using a small lab scale pyrolysis reactor, approximately 200g of palm kernel shell sample with dried moisture content of less than 10% was packed in the reactor and pyrolysed. The experimental process occurred in a cylindrical glass container with a sample loading chamber 8cm outside, 7cm internal diameter and 64.2cm length heated in an external muffle furnace. The temperature was controlled by a thermostat (Lauda low temp thermostat RE 207). The products of the pyrolysis process is recovered using two series of water cooled condensers connected to a water cooling system. This process occurred in the absence of oxygen using a nitrogen flow [10]. The pyrolysis process resulted in the production of a solid product of char, a liquid product and some non-condensable gases. The quantities of char produced were determined by weighing after the pyrolyser was allowed to cool for at least 24 hours. The weight of the non-condensable gases is determined by difference. The mass yield is determined by the formula

$$Y_p = \frac{W_p}{W_{pks}}$$

where$Y_p$is the product yield, W_p is the weight of the product andW_{PKS}istheweight of the palm kernel shell.

Physiochemical Properties of Pyroligneous Acid Product

The pH and density of the pyroligneous products evaluated. The pH meter is used in measuring the level of acidity of the product.

RESULTS AND DISCUSSION

The study intended to investigate the relationship between product yield (solid, liquid and gases) with much emphasis on the pyroligenous acid product (liquid), residence time and temperature. The utilization of biomass is very promising as a substitute of fossil materials which can be used in energy applications and also in many other applications. From Table 1, the ultimate analysis of the samples from the five palm oil mills analysed. All the samples were found to be high in carbon content and low in sulphur and nitrogen making good fossil fuel substitutes. Sample 4 was found to have the highest carbon content, low sulphur and nitrogen content thus the sample was chosen for further studies.

Table 1: Ultimate analysisof five different oil mills

Samples	Content Weight %				
	C	H	N	S	O
1	48.569	7.163	1.025	0.085	40.844
2	45.770	7.173	0.942	0.056	46.100
3	47.425	7.505	1.006	0.053	44.011
4	49.592	7.752	1.060	0.032	41.564
5	48.779	7.649	1.169	0.059	42.344

The PKS samples are found to be high in volatile content and low amount of fixed carbon. From the proximate analysis, the ash contents appears to be low in some samples. The ultimate/elemental analysis results indicate that PKS samples are carbon and oxygen rich with low levels of hydrogen and trace quantities of nitrogen and sulphur. To express the suitability of biomass for thermochemical conversion, high volatile matter content of biomass with low sulphur and ash content is the main criterion for thermochemical conversion of biomass should be taken into consideration [5].

Table 2: Proximate and compositional analysis of five different oil mills

Samples	Proximate Content Weight %			Compositional Analysis		
	Moisture	Fixed Carbon	Volatile	Ash	Lignin	Extractives
1	6.27		91.42	5.10	40.87	8.16
2	7.50	0.73	s86.29	6.57	48.89	3.90
3	6.60		89.24	3.43	45.51	7.11
4	7.10		90.24	2.73	44.98	9.15
5	5.90	0.99	90.24	2.47	43.90	9.50

The results from Table 1 and 2 show the ultimate, proximate and compositional analysis of the different samples. The sample utilized for further research were chosen based on the results of the analysis. From the above table, with the high lignin content (the lignin content being considered as a potential source of chemical) and low ash content (composition of oxides and sulphates) given consideration.

The composition of the biomass (cellulose, lignin and hemicellulose) and operational parameters (final temperature, heating rate and residence time) affect the final composition of the products (content and the characteristic).These two factors interact during thermal degradation of biomass [11, 8]. The biomass samples were tested at different temperatures and the composition and yield of products recorded, the difference in yield from (Table 3).

Table 3: Comparisonof pyrolysis product yield for various pyrolysis temperature

Temperature(^{0}C)	419^{0}C	429^{0}CRT 35	429^{0}CRT 39	439^{0}C	529^{0}C
PA	59.64	61.52	80.97	69.82	76.64
Char	79.89	79.91	73.58	77.03	64.29
Gas	61.11	58.57	45.69	53.83	59.31
Mass yield %	30.46	30.62	40.44	34.79	29.62

*rt-residence time

The highest mass yield of 40.44% was observed at heating temperatures of 429^{0}C with residence time of 39^{0}Min. According to [13] about the duration of time, the pyrolytic products remain in the reactor before being discharged out of the reactor chamber. The residence time has an influence on products of pyrolysis.The effect of the residence time is evident when the heating rate is increased to 39^{0} Min. The mass yield of pyrolytic product is increased, while the char and gas yield decreases with increase in retention time.This agrees with previous research of [6].

Table 4: Comparison of pyrolysis product yield for various pyrolysus temperature

Temperature (^{o}C)	419^{o}C	429^{o}CRT 35	429^{o}CRT 39	439^{o}C	529^{o}C
Heating rate	**1.34^{o}C/Min**	**1.34C/Min**	**1.34^{o}C/Min**	**1.34^{o}C/Min**	**1.34^{o}C/Min**
Residence time	39^{o}Min	39^{o}Min*	35^{o}Min*	39^{o}Min	39^{o}Min
Mass yield %	29.82 %	40.44%	30.62%	34.79%	29.62%
pH	3.58	3.77	3.37	3.36	3.36
Density	1.017g/ml	1.014g/ml	1.023g/ml	1.021g/ml	0.861g/ml

*Different residence time

The values shown are the average of three runs.

CONCLUSION AND RECOMMENDATIONS

Pyrolysis of PKS samples at different temperature and resident time resulted with the highest yield of liquid pyroligneous acid at temperature range of 429^{o}C.All three different products of pyrolysis produced (solid product of char, liquid product of pyroligneous acid and non-condensable gaseous products) which could be further utilised. The pyrolysed products can be applied in various fields and for different industrial uses. The char used in production of activated carbon, energy generation, the gases in energy generation. The pyrolysed acid products are rich in targeted phenolic compounds also other bioactive compounds present in the pyroligneous acid could be further studied to develop novel applications in energy, food and pharmaceutical industries that can bring great contribution to the society. Palm kernel shell biomass is waste found in abundant quantities polluting the environment all over the world which can be utilized through the process of waste management and treatment to extract potentially viable nutrients for drugs and supplement productions for health improvement as well ensure sustainability in oil palm industries.

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