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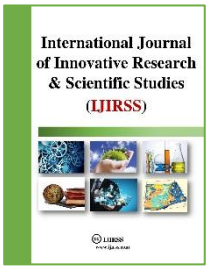
International Journal of Innovative Research and Scientific Studies, 1 (2) 2018, Pages: 34-39

IJIRSS
International Journal of Innovative Research & Scientific Studies

Received 27 March 2018
Accepted 16 April 2018
Available online 14 October 2018

ISSN: 2617-6548

www.ijirss.com



Research Article

Effect of temperature on bio-oil fractions of palm kernel shell thermal distillation

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Abstract

Distillation is an essential thermo chemical process; it mainly depends on temperature which affects mostly the product yield and composition. The aim of this research is to investigate the effect of temperature on the characterization of bio-oil liquid fraction derived from palm kernel shell (PKS) bio-oil. The temperatures were 100 °C and 140°C. The higher heating value (HHV) obtained were 28.6MJ/Kg and 31.5MJ/Kg for bio-oil fraction 100°C and 140°C respectively. The GC- MS analysis determined that phenol is the dominant product in bio-oil fractions.

Keywords: Fast pyrolysis, thermal distillation, palm kernel shell, biomass, bio-fuel

1. Introduction

In today's world, almost 81% of the total transportation fuels are prepared by petroleum. The depletion of natural resources (non-renewable sources) is an important issue and attention needs to be paid to it. The air contamination is a wide problem in the world also and it is formed from the internal combustion of fuel that produces greenhouse gases such as CO and SO_2 stable released to the environment. Biomass is an alternative energy source for crude oil. Biomass commutation to bio-oil comprises two processes; flash pyrolysis and hydrothermal liquefaction. The main challenges are the low product, negligible bio-oil quality and the value of bio-oil commutation from biomass [1]. Biomass is an accessible, low-value and renewable reserve, which has received consideration due to its multiple characteristics. It is a renewable energy that can be changed into bio-fuel by different methods such as pyrolysis, gasification, combustion, and liquefaction. These methods are conventional and the disadvantages of these methods are

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higher temperature, long processing time, and usage of catalysts [2,3].

Fast pyrolysis using palm kernel shell (PKS) is one of the methods that can improve the properties of the biomass to the next level of advancement. The pyrolysis is conducted at a temperature of about 500ºC with vapor residence of 30 minutes. The pyrolysis feedstock used wood, waste, empty fruit bunch (EFB), and PKS, with a bio-oil yield of 70%, and char and gas at around 15%, each [4]. Pyrolysis is dependent on the thermo chemical process. Bio-oil is a liquid fuel that burns in diesel engines or boilers and it is of high density and oxygenated liquid [5]. Therefore, bio-oil from fast pyrolysis application as fuels or sources of chemical feed stock requires some form of thermo distillation to improve storage stability and heating value [6]. Thermo distillation of fast pyrolysis bio-oil can be a good enhanced process. However, oxygenated components can polymerize. In conventional distillation, relatively high temperature is necessary [6]. Bio-oil is a product of fast pyrolysis obtained by means of distillation. The experiment operates at a temperature of 100oC, 140 oC and residual pressure of 15mmHg. The distillation of bio-oil has low oxygen content, about 9.2 wt% than fast pyrolysis' product and the bio-oil produced from distillation has lower corrosively but higher heating value and stability. After distillation, the bio-oil heating value becomes higher, that is 34.2 MJ/kg, and the value is twice higher than that of a fast pyrolysis [7].

PKS is the waste; it is obtained after the production of palm oil from the broken nuts. The kernels are removed with the shell essentially left as waste. PKS has different shapes and sizes, and the hard, stony shell is covered by the kernel. The shell compounds are made of 33% charcoal, 45% pyroligneous liquor and 21% combustible gas as reported [8]. PKS has higher calorific value, lower sulfur content and can be found easily. The bio-oil which was produced from PKS and also distilled bio-oil fraction was characterized in terms of physical and chemical properties Therefore, to reduce the instant fossil fuel greenhouse gases, the conventional fuel needs to be replaced with organic crude fuels (unconventional fuels). To reduce the instant fossil fuel greenhouse gases, the conventional fuel needs to be replaced with organic crude fuels (unconventional fuels) [9]. Hence, the aim of this study is to investigate the effect of temperature on bio-oil fractions of palm kernel shell thermal distillation to find alternative fossil fuel. Distillation is a suitable method to improve the bio-oil of fast pyrolysis. Oxygenated components can polymerize with this method. In conventional distillation process high temperature is necessary. Therefore, thermal distillation of fast pyrolysis of bio-oil is performed to improve the storage, stability, and heating value of fast pyrolysis bio-oil [6].

2. Materials and Methods

2.1. Feedstock and chemicals

The raw material used in this research is palm kernel shell that was collected from a palm oil mill industry located in Klang, Selangor, Malaysia. The nitrogen gas was supplied by the UiTM laboratory and was used in the pyrolysis process. The particle size of PKS was 10-30 mm. The bulk density was around 560 kg/m3. As shown in Fig.1. The moisture content obtained from the sundried PKS was around 12 wt%. The major weight loss is different for EFB (57 wt%) and PKS (52 wt%), whereby they are both lower than sawdust's weight loss (67wt%) [10].

Fig.1. Raw material PKS.

The bio-oil chemical and physical properties primarily depend on chemical and physical properties of the raw material as well as reaction conditions of pyrolysis. The physical and chemical properties of PKS were provided with proximate and ultimate analysis. Table 1 shows the chemical and physical properties of PKS. The PKS particle size was between 10-30 mm, the bulk density of PKS was 560Kg m-3, while the PKS

moisture content was 12 wt. %. The proximate analysis of PKS showed the percentage of the volatile fraction, fixed carbon and ash content, were recorded at 52wt%, 24wt% and, 16wt% respectively. In addition, the ultimate analysis of PKS provided the hydrogen, oxygen and carbon content, that were 5.4wt%, 44.8wt% and, 49.8wt%, respectively.

Table 1. Chemical and physical Characterization of PKS

Properties	PKS
Particle size (mm)	10-30
Bulk density (Kgm^{-3})	560
Moisture content (wt%)	10
Calorific Value (KJ/KG)	17.092
Proximate analysis(wt%, dry basis)	
Volatile fraction	52
Fixed carbon	24
Ash content	16
Ultimate analysis(wt%, dry basis)	
C	49.8
H	5.4
O	44.8

2.2.Procedure of bio-oil production

The bio-oil production has been pyrolyzed in UiTM's laboratory scaled fixed bed reactor. The reactor was positioned in vertically and it made of stainless steel with the size of 10 cm i.d and 50 cm height. Around 2kg of the biomass was the feedstock, placed in a batch reactor. The nitrogen gas was injected a mount 200ml/min inside the reactor from the bottom to replace the air from the reactor with the gases formed from the pyrolysis of the biomass inside the reactor. There were two condensers the first condenser was cooled using dry ice, which was the vapor temperature reduced to around 60°C, and the second condenser was cooled by the circulation of ice water, the temperature reduced around 5°C [10].

2.3. Distillation of bio-oil procedure

The method used to upgrade the bio-oil is via a reactor and stirring hotplate that will assist the distillation process through some modifications made. Firstly, the bio-oil placed inside the reactor and heated at about 100°C with stirring hotplate. Finally, 10 fractions were collected.

2.4. Analytical methods

The physical characteristic of bio-oil and bio-oil fractions was determined including the PH value, higher heating value, moisture content, density, and ultimate analysis. Densities of bio-oil and bio-oil fraction were measured at 25°C by using the hydrometer. The pH of bio-oil and bio oil fractions was measured by digital PH meter Toledo ™. The higher heating value was estimated via bomb calorimeter. The bio oil and bio oil water content were measured by water analyzer (satorius ™ Model- MA35). All the analysis is shown in Table 3. The bio-oil and bio-oil fractions functional groups determined by FT- IR spectroscopy. The FTIR spectra of bio-oil and fraction of bio-oil utilized perkin-Elmer Spectrum GX FT- IR spectrometry, and the wave number were between 4000- 400 cm-1. At 4-1spectrl resolution fifty scans were recorded [11]. The Gas chromatography- mass spectroscopy (GCMS) analysis of bio-oil fractions as has shown in Table 2. Phenol and its derivative were the highest values of the peak areas of possible compounds. The condensation of phenol and its subsidiary were found very high which demonstrate the appropriateness of the oil to be observed for value-added chemical [12].

3. Results and discussion

The chemical and physical characteristics of feedstock play an important role in the yield properties. Therefore, the PKS raw material bio-oil and bio-oil fraction were characterized to know the chemical composition and physical properties, as shown in Table1 and 3 .First, the biomass has around 50wt% moisture; however, after drying in the dryer for 48 hours, it is reduced around 20 wt%, for the biomass and 10 wt% for the bio-oil respectively.

The bio-oil fractions have higher water content it is due to the high moisture content of the feedstock. Surface area and particle size play an important role on the yield content. Thus, the particle size was 8- 12 mm it crushed with grinding machine [13]. The calorific value

of bio-oil was 20- 21 MJ/Kg [14]. The bio-oil density was 1.04 g/mL at 25°C. The bio-oil fractions pH were between 2.52- 2.67. The bio oil fractions densities were 298 wt% and 994.56 wt%. The HHV of bio oil fractions were for PKS100°C around 28.6 MJ/Kg and for PKS 140°C was around 31.5 MJ/Kg. The bio-oil fractions energy content were more than half of the diesel energy content 43.09 MJ/Kg, it is still a considerable amount of energy.

3.1. Chemical analysis of bio-oil and bio-oil fraction

The FTIR spectroscopy PKS bio-oil as shown in Fig.2 indicates that the bio-oil consisted oxygenated organic compounds. The broad bond between 3360-3600cm-1 indicates the O-H stretching vibration proves the presence of phenol and alcohol. The C=O stretching vibration between 1699- 1710 cm-1 indicated the presence of the conjugated aldehyde. The stretching vibration between 1637- 1650 cm-1 indicated the presence of an aromatic group. The C=C stretching vibration between 1501- 1510 cm-1 indicated the presence of which indicated the presence of alkenes. The C-O, C-C stretching vibration between 1474- 1475 cm-1 indicated the presence of Alkanes, alcohol, phenols, ethers and lipids [15,16]. The C=C stretching vibration between 1379- 1450 cm-1 which indicated the presence of mono and polycyclic substituted aromatic group [17]. The C-O stretching vibration between 1263- 1300 cm-1 which indicated the presence of alcohol [18]. The C-O stretching vibration between 1015 and 1200 cm-1 which indicated the presence of carbonyl component [16].

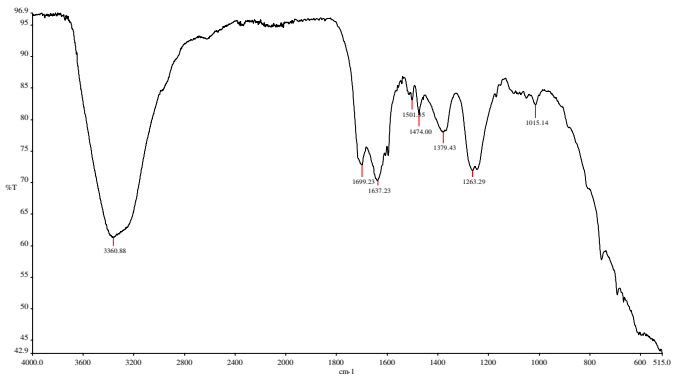

Fig. 2. FTIR spectra of bio oil

GCMS analysis was carried out with typical bio-oil fractions and determined type of possible compounds and nature in the bio-oil fractions. The bio-oil fractions possible compounds were identified by the MS search libraries.

The possible compounds of bio-oil fractions are listed in Table 2. GCMS analysis result shows that the Phenol derivative is the major group of compounds existed in bio-oil fractions. Most of the compounds were oxygenated compounds.

Table 2. Possible Chemical Compounds of bio-oil fractions according to the GC-MS Analysis

Possible Chemical compounds	Molecular formula	Area, %
Furfuryl hexanoate	$C_{11}H_{16}O_3$	4.31
Idazoxan	$C_{11}H_{12}N_2O_2$	2.12
1-(Trimethylsilyl)-1-propyne	C_6H1_2Si	2.12
4-Picoline	C_6H_7N	9.83
Idazoxan	$C_{11}H_{12}N_2O_2$	9.83
Benzene,(1,1dimethylethoxy)	$C_{12}H_{16}O$	9.83
Phenol, 4-methyl	C_7H_8O	1.42
1,4:3,6-Dianhydro-à-d-glucopyranose	$C_6H_8O_4$	9.54
1,4-Benzenediol, 2-methoxy	$C_7H_8O_3$	8.17
Phenol, 3-nitro	$C_6H_5NO_3$	2.91
Propan-2-one,1-(4-isopropoxy-3-methoxyphenyl)	$C_{13}H_{18}O_3$	1.05
Dodecanoic acid, isooctyl ester	$C_{20}H_{40}O_2$	6.81
Dodecanoic acid	$C_{12}H_{24}O_2$	6.81

Oxygenated compounds decrease the HHV and also decrease the quality of bio-oil and bio-oil fractions to be used as fuel utilization and transportation. However, the oxygenated compounds reduce is still possible. These components need some methods to reduce the oxygenated compounds such as hydro treating and hydro cracking.

Table 3. Properties of bio-oil and bio-oil fractions

properties	Bio-oil fractions				Bio-oils	
	PKS - 100	PKS – 140	EFB – 100	EFB – 140	PKS	EFB
Moisture content (wt%)	21.35	13	23.82	18.47	40- 60	30- 40
PH	2.67	2.52	3.12	2.95	3.5	3
Density (wt%)	982	994.56	994.56	970.59	1040	1040
Elemental analysis						
C	56.30	64.63	56.7	60.2	40- 50	40-45
H	7.2	7.3	6.89	7.1	5.0- 6.0	4.0- 5.0
O	36.18	27.81	36.16	32.45	40- 50	45-50
N	0.19	0.15	0.11	0.11	0- 0.2	0.02
S	0.13	0.11	0.14	0.14	<0.001	<0.001
HHV	28.6	31.5	22.7	25.4	16.74	17.09

Conclusions

PKS bio-oil fraction was produced from thermal distillation at 100°C and 140°C. The higher heating value of bio-oil fractions determine by bomb calorimeter. The bio-oil fraction component in 140°C compared with bio-oil fraction in 100°C. The component fraction in 140°C was perfectly ignited. The PKS bio-oil in 140°C will be considered as bio-oil to be used in the future.

Acknowledgment

Authors would like to thank faculty of chemical engineering (FKK), and Research management institute (RMI) in UiTM for providing funds (600-RMI/DANA 5/3/BESTARI0008/2016) that made this research possible.

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