Production of Bio-fuels by microwave-assisted Rapid Hydrothermal Liquefaction of Palm Kernel Shells Biomass

A A. Saleh

Universiti Malaysia Sarawak

Md Saiful Islam (✉ msaifuli2007@gmail.com)

Bangladesh Army University of Engineering and Technology

Md. Shaharul Islam

Bangladesh Army University of Engineering and Technology

M. A. M. A. Banggan

Universiti Malaysia Sarawak

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Abstract

Hydrothermal Liquefaction (HTL) process is an alternative way for converting biomass to bio-fuels product. The aim of this study was to determine the effect of sample's mass and heating time on the product yield (wt%) from palm kernel shells (PKS) and to characterize the bio-oil as produced. PKS which is one kind of biomass efficiently converted to bio-oil, bi-char and bio-gas by HTL associated with modified microwave oven. A modified household microwave oven with 800W was employed in this process. The product yield was increased proportionally with the sample mass from 31.16 wt% to 41.92 wt% for bio-oil at constant time of 15 minutes. However, a vice versa trend was observed for bio char. Furthermore, it was exhibited that the highest value of 66.51 wt% and then it reduced to 42.17 wt%. The last product, bio gas shows an increasing trend from 2.32wt% to 15.90wt%. For the second parameter, the production of bio oil decreases with the increasing of heating time while bio char and bio gas increases with the increases of time. For the highest product yield, the calorific value is 37.68 MJ/kg for 15g sample and 22.32 MJ/kg for 35g sample at 15 minutes heating time. Fourier Transform Infrared Spectroscopy (FTIR) result reveals that multiple functional groups i.e. alcohol, aldehydes, carboxylic acid and ketones is present in the PKS bio oil. Additionally, the pH value of the bio oil was in the range of 2-3.

Introduction

Energy is crucial in our life to fulfill the demand in power generation and provide light/heat sources to mankind. In current years, the increasing amount of CO₂, SO_x and NO_x emission has become a major concern on the consumption of the world energy [1]. For the limited availability of fossil fuels and high level of air pollution, the importance of energy efficient technologies are increased, and gasification, being a highly proficient technology, has received considerable interest [2]. At present, coal is the key feedstock in gasification and is expected to be applied as the energy reserve for many decades ahead. On the other hand, this direction is hard to achieve due to the increase in energy demand that had caused the lack of supply and reduction of coal [3]. However, non-renewable energy causes negative impact for the past few years in term of pollution. Thus, development of new, clean and renewable-energy is the alternative way to solve this issue. Consequently, one of the approaches is to utilize the biomass in thermo chemical conversion such as pyrolysis, liquefaction, and gasification. The traditional use of biomass has been restricted to cooking and heating purposes, which has affected adverse impacts such as land degradation and desertification. However, the recent use of biomass with a high-quality energy carrier transformed from raw biomass for electricity and heat production can substantially reduce emissions from the conventional power plants. This ability to exchange raw biomass into convenient energy carriers increases the attention on biomass use for energy purpose, particularly the lignocellulosic biomass [4]. Biomass is one of the competent renewable energy sources and is applied as solid, liquid, and gas fuels [5, 6]. The biomass is an attractive concern worldwide, because of its non edible quality, carbon neutrality, and relative abundance. Moreover, the increasing worries about the effects of CO₂ emissions from fossil fuels call for sustainable energy sources, such as biomass [7].

In Malaysia, oil palm residues are considered to be the most abundant biomass and the greatest prospects for fuel generation. Malaysia produces about 47% of the world's palm oil source and can be reflected as one of the world's largest producers of palm oil. Therefore, Malaysia produce large quantity of oil palm biomass including palm kernel shell (PKS), oil palm trunks, oil palm fronds, empty fruit bunches, and fibers as residues from harvesting and processing activities [8]. The PKS as one of the residues from oil palm industry generated about 4.19 MnT in 2016 [9]. Therefore, PKSs appear to have outstanding capacities to become an alternative source of energy for the country. However, the choice of conversion methods suitable for a particular type of biomass and the target fuels becomes a challenge because of the complex three-dimensional (3D) structure connecting the main biomass components (i.e. lignin, cellulose and hemicellulose). This structure supply strength to the materials, and offers resistance that protects them against chemicals and microbial attack making it very complicated to hydrolyze. An effective decomposition of these components and their subsequent partition are needed for the production of high value products from lignocellulosic biomass [10]. One potential approach introduced recently is "hydrothermal liquefaction method" or commonly referred to as "hydrothermal upgrading". HTL basically a pressure cooking that produces liquid bio-crude at high pressure of 50–200 atm with moderate temperature of 250–400°C approximately 20–60 minutes. A number of review articles of the technique have also been published in recent times including the comprehensive review of the technology summarized by Peterson et al. [11]. Reviews on its application to different biomass components such as protein, carbohydrates, lignin and fats have also been reported [12, 13, 16]. The hot-compressed water has also been compared with other hydrolysis methods [17] and shows it to be very attractive economically and environmentally due to higher sugar revival even in the absence of acid and chemical catalysts. The growing popularity of this method is due to the deemed incredible opportunities that biomass of any sources can offer as energy carrier, united with the promising properties of water at high temperature and high pressure, especially under sub- and supercritical conditions. Malaysia is one of the growing agricultural countries in the world, producing main agricultural crops such as oil palm, rubber, cocoa, rice and coconut [18].

Microwave technology utilizes electromagnetic waves for heating as a result of friction formed by oscillation of molecules as they realign with microwave upon absorption. Microwaves work in between infrared radiation and radio frequencies of 30 GHz to 300 MHz, parallel to wavelengths of 1 cm to 1 m. Strict government regulations only allow domestic and microwave apparatus to operate at either 122.2 cm (2.45 GHz) or 33.3 cm (900 MHz) to avoid interference with RADAR transmissions and telecommunications [19]. Using microwave, rapid heating occurs as a result of heat being generated within the material, unlike the usual method where heating of material is performed by conduction from heat sources outside of the vessel. Many microwave-assisted reactions are accelerated due to this rapid internal heating, resulting to incredible increase in reaction rates compared to the conventional methods. Thus, even at shorter reaction times, higher yields and selectivity of target compounds are expected. Some other reactions not possible with the conventional heating methods had also been reported to proceed by microwave irradiation. The available information related to the fundamentals of microwave chemistry in sample preparations and other applications had been summarized by Haswell [20]. Bio oil is

a dark, viscous liquid with the same element composition of biomass and made up of many oxygenated organic compounds. It have large water content (15–20%) that use to suspend hundred different molecules called 'micro-emulsion' and reducing the emission of nitrogen gas (NO_2) and sulfur gas. Bio oil is used to replace non-renewable energy source because it completely renewable, produce no carbon dioxide and sulfoxide emissions. Besides, energy produce is much cleaner than fossil fuel-generated energy and has higher viscosity compared to diesel oil. The exact conversion of biomass to bio-oil is dependent on several variables which are feedstock composition, temperature and heating rate, pressure, solvent and residence time. The advantage of Hydrothermal Liquefaction (HTL) is it can process wet biomass and enable to produce bio-oil that contains twice the energy density of pyrolysis oil which makes it differ from pyrolysis process. During the conversion of biomass to bio-oil, water is used as a medium in which the reaction occurs, acts as reactant, solvent and catalyst for the process. Besides, water is a green and environmentally benign solvent, non-toxic, nonflammable, cheap and more importantly, it was naturally present in biomass [21]. Typical pyrolysis processes required water content less than 40% to convert biomass to bio-oil which increases the heat of vaporization of the organic material. Since bio-oil is extracted from feedstock such as kernel shell, corn, microalgae and plants, so gaining these organic materials is a new challenge. Many research works related to bio oil productions from various biomasses has been carried out by various researchers, however; very little work, so far no work is conducted on bio-oil production from Malaysian Palm Kernel Shell (PKS). Therefore, the aim of this study is to develop a rapid Hydrothermal Liquefaction process supported by microwave irradiation for efficient conversion of Palm Kernel Shells to bio-oil and bio char and to characterize bi-oil properties for renewable energy sources.

Materials And Methods

The agricultural waste sample was used for this research is palm kernel shells (PKS). The sample was collected from Samarahan KPF Palm Oil Mill Sdn. Bhd., Sarawak with approximately size of 212-300 μm , 300-600 μm , 600 μm -1.18mm and 1.18-2.36 mm.

Experimental Set-up

Household microwave oven (Panasonic NN-ST342M) was modified for the hydrothermal liquefaction (HTL) experiment of agricultural waste (PKS). A 40 mm diameter hole was made through the top part of the microwave oven for attaching the Quartz Reactor. With diameter 40 mm and height 250 mm, the Quartz Reactor is in tube size and clamped using retort stand.

The experiments was done by placing PKS into quartz first then followed by placing into the microwave oven. 1000 W input power was set for microwave oven with frequency 2450 MHz. To measure the temperature of samples, thermocouple was used and monitored by digital multimeter. T-shaped connector with C24/29 is used to connect the Quartz Reactor's gas outlet with Liebig Condenser. Tap water acts as cooling medium for Liebig Condenser. 3 necks collecting flask was connected to the other

end of Liebig Condenser by L-shaped connector with socket C24/29. Figure 2 shows the schematic diagram of the experimental set up.

Experimental Procedure

The PKS sample is crushed into small particles by using Crusher and then it was sieved using a sieve shaker to separate the particle sizes needed. Aluminum foil is used to cover all the holes to avoid gas leakage during the experiment. Then, the experiments was continued by placing 15 grams of the samples in quartz reactor and placed into heating mantle with optimum heating temperature is 250-400 °C. The HTL yield results from the various parameters of the process were investigated by identifying the HTL process time in 15 minutes, 30 minutes and 45 minutes. The carbonaceous residue (char) that can be obtained directly from quartz reactor is weighed to calculate the percentage of the yield. Besides, fractions of the solid and oil yields were calculated based on weight. Gas yield can be calculated by weight difference. As the experiment done, dichloromethane was used to wash the deposited bio-oil at condenser and equipment. 3 necks collecting flask used to collect volatiles substances.

Digital multimeter is used to monitor the sample's temperature during experiments. The result was seen on modern digital multimeter by attaching the thermocouple on the digital multimeter. Thermocouple is used to attach inside round flask before beginning the experiment to measure heating temperature. During the experiment, the optimum temperature was considered. Figure 5 show the modern digital multimeter with thermocouple.

The bio-oil, char and biogas were weighed to calculate the percentage of the yield.

Bio-oil yield Measurement

The yield of liquid fraction is determined. Weight of sample waste inside reactor before HTL experiment was measured whereas weight of liquid products was measured after HTL experiment. The following equation shows the yield of bio oil, Y_l

$$Y_l = W_l / W_s \times 100\%$$

Where W_s = Weight of waste sample before HTL and W_l = Weight of liquid product produced by HTL.

Bio char Yield Measurement

Weight of material was measured before and after experiment. The following equation shows the yield of bio char, Y_s .

$$Y_s = W_c / W_s \times 100\%$$

Where W_s = Weight of sample before HTL and W_c = Weight of sample (bio char production) after HTL

Biogas yield Measurement

The non-condensable gas yield, Y_g can be calculated by following equation.

$$Y_g = 100\% - Y_s - Y_l$$

Where Y_s = Yield of bio char and Y_l = Yield of bio-oil.

Analysis of Bio-oil

The functional groups present in the bio-oil obtained at optimum conditions were identified using Fourier transform-infrared (FTIR) spectroscopy. A Magna-IR550 Nicolet Madison Spectrum series II FTIR device with a resolution of 1.0 cm^{-1} was used to investigate the functional groups presents in the bio-oil within the range of 400 cm^{-1} to 4000 cm^{-1} . The calorific value of bio-oil sample was measured by Bomb Calorimeter and the pH of the sample was tested using pH paper (Universalindikator Merck).

Results And Discussions

Effect of Sample Mass on Product Yield

The effect of pyrolysis time and sample mass on the yield of the pyrolysis product was investigated. Three different types of sample of mass 15g, 25g and 35g have been investigated. The overall product yield (wt %) of Palm Kernel Shell at different holding time and mass were analyzed and shown in figure 6, 7 and 8 respectively.

From Figure 6, 7 and 8, it was observe that the maximum bio oil yield for Palm Kernel Shell is 41.9257% for 35g sample at 15 minutes whereas the minimum yield is 23.2733% for 15g sample at 45 minutes as seen in figure 8. Besides, bio char is also produced under this process. From figure 6, it can be found that the maximum yield of bio char produced is 66.5133% at 15 minutes for 15g sample. While, the lowest yield of bio char is 42.1743% for 35g sample at 15 minutes. The final product is bio gas and it was hard to determine the exact amount of bio gas produced and therefore the percentage of gas yield was calculated with the difference biomass feedstock and the combination of bio oil and char. The maximum gas yield is 16.9467% at 45 min for 15g sample while the lowest yield is 2.32670% at 15 min for 15g sample. Bio char yield was decreased sharply due to the heat provide to the process as the lignocellulosic materials of the biomass was decomposed by endothermic reaction. This result was also confirmed by Asadullah et al. using PKS biomass [22]. The increases of bio gas yield due to the release of volatile matter from the destruction of organic composition of material during heating. For this reasons different products have different graph trend.

Effect of Heating Time on Product Yield

The heating time investigated in this research was 15 minutes, 30 minutes and 45 minutes. From Figure 9, it is observed that the bio oil yield is decreased from 31.16 wt% to 23.2733 wt% as the heating time increased. The bio oil yield decreases due to the long retention time of the sample during heating which is

agree with the observation of J. O. Ogunkanmi et al [23]. Long HTL time could increase the bio oil yield but when it will reach the upper limit, it could decrease the bio oil yield as the cracking, and polymerization reaction occurred.

When microwave heating time keep increasing, the bio char shows a fluctuate trend which decreases from 66.5133 wt % to 56.6867 wt % and then increases to 59.78 wt %. While for bio gas it is shows an increasing trend from 2.3267 wt % to 15.72 wt % and then to 16.9467 wt %. This is because most of the gas become non-condensable and run out from the condenser. High yield of bio gas attributes to secondary cracking of volatile matter. So, it is necessary to obtain a suitable heating time based on the experimental data.

Identification of functional group using FTIR

The FTIR spectrum of the bio-oil obtained from pyrolysis of palm kernel shell for 35g sample at 15 minutes is shown in Fig. 10.

From the FTIR result, O-H stretching is observed at range of 3200 - 3600 cm⁻¹ and contains Phenols and Alcoholic compound. There are many peaks also at this range which means that bio oil consist of higher oxygen content. The presence of alkanes was found at peak of 2850-3000 cm⁻¹ and 1370-1480 cm⁻¹ when the C-H stretching was occurred. The C=O stretching vibrations between 1628 and 1815 cm⁻¹ represent the presence of ketones, aldehydes, carboxylic acids and their derivatives. The absorbance peaks between 1470 and 1620 cm⁻¹ represent C=C stretching vibrations indicative of alkenes. Absorptions possibly due to C-O vibrations from carbonyl components (i.e., Phenols, esters) occur between 1000 and 1370 cm⁻¹ of the analyzed bio-oil. The absorbance peaks between 669 and 915 cm⁻¹ indicate the possible presence of single, polycyclic and substituted aromatic groups. These results agree with chemical compositions reported in literature consisting of several hundreds of organic compounds, such as acids, alcohols, aldehydes, esters, ketones, phenols and lignin derived oligomers [24].

Analysis of Calorific Value

Bomb Calorimeter was used to determine the High Heating Value (HHV) for the highest yield of bio oil sample.

Table 1: Calorific Value of Highest Bio Oil Yield

Bio Oil Sample	Calorific Value (MJ/Kg)
15g at 15 minutes	37.6790
35g at 15 minutes	22.3157

From Table 1, it is shown that 15g of sample have high calorific value compared to 35g sample at constant time. Higher oxygen content will lower the calorific value as oxidizable compounds are hard to

oxidize at higher oxidation stage. As the microwave power level increased, the O/C ratio of torrefied PKS is gradually reduced as more volatile matter is being released as a result of the continuous decomposition. The reduced atomic ratios is also indicates the extent of conversion efficiency and oxidation degree of pretreated products [25]. Besides, high moisture content decreased the calorific value of bio oil.

Measurement of pH

At last we have conducted the pH test. Figure 11 shows the results of the test.

From the Figure 11, it is found that the bio-oil obtained from PKS have a pH value in the range of 2-2.5 which agree with the common values (~2.5) for bio-oil and lower from the observed value (3.70 - 4.32) [26, 27]. The Presence of acetic acid and formic acid in bio-oil during HTL process is responsible for the low pH value.

Conclusions

It can be concluded that Palm Kernel Shell (PKS) has been efficiently converted to bio-oil, bi char and bio gas by HTL supported by modified microwave oven. The bio oil yield increase with the increasing of the sample's mass of PKS but an opposite result was observed for the heating time. On contrast, the yield of bio char and gas is found to be decreased with the increases of sample mass. Heating time was inversely effected to the yield of bio oil. Besides, calorific value for the highest product yield decreased with the increasing mass of sample. The FTIR results revealed that the bio-oil composition was dominated by oxygen containing compounds and the low pH value indicates the acidic nature of the bio oil obtained from PKS. The authors proposed that the biomass yield from PKS is affected on the few factors such as reaction time, type of biomass used and temperature.

Declarations

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Conflicts of interest: No conflict of interest.

Declarations: Not applicable.

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Figures

Figure 1

The collected sample of Palm Kernel Shell.

Figure 2

Hydrothermal liquefaction experiment of Palm Kernel Shell supported by microwave irradiation (1- Microwave oven, 2-Quartz Reactor, 3-Thermocouple, 4-T-shaped connector, 5-Liebig Condenser, 6-L-shaped connector, 7-3 necks collecting flask).

Figure 3

Flow sheet of PKS that undergo rapid HTL process

Figure 4

The modern digital multimeter with thermocouple

Figure 5

Experimental set-up of Hydrothermal Liquefaction Process.

Figure 6

Product yield for different sample mass at 15 minutes.

Figure 7

Product yield for different sample mass at 30 minutes.

Figure 8

Product yield for different sample mass at 45 minutes.

Figure 9

Effect of Heating Time on Product Yield.

Figure 10

FTIR testing result for 35g sample at 15 minutes.

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