

An Exploration of Modified Microwave-assisted Rapid Hydrothermal Liquefaction Process for Conversion of Palm Kernel Shells to Bio-oil

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ABSTRACT

Bio-oil is one of the potential resources to address the sustainable energy development and environmental issues. Microwave-assisted Rapid Hydrothermal Liquefaction Process is one of the popular techniques that is used to extract bio-oil from biomass. In this paper, the bio-oil has been extracted from Palm Kernel Shells by using microwave-assisted and conventional heating pyrolysis processes. A modified heating mantle apparatus are used to conduct the experiment for extracting the bio-oil. The experiments are conducted by varying the hydrothermal temperature and time for both techniques to achieve the conversion of the bio-oil from the raw material. It is found that the yield of bio-oil for microwave-assisted Rapid Hydrothermal Liquefaction Process at 350°C and 400°C are from 10.70 wt% to 25.60 wt% within hydrothermal time 6, 9 and 12 minutes. The pH value of the bio-oil is acidic with the range from 3 to 4. The calorific value of the bio-oil is varied from 24 to 26 MJ/kg for both conversion methods. Fourier Transform Infrared Spectroscopy (FTIR) result reveals that multiple functional groups (alcohol, aldehydes, carboxylic acid and ketones) are present in the PKS bio-oil.

Keywords: Biomass; Hydrothermal; Bio-oil; Microwave; Heating value

1 INTRODUCTION

Energy is one of the basic needs for economic growth, automation and modernization. There have been raising concerns about the world's use of fossil fuels with the increase in energy consumption. In addition to the industrial growth and standard of living, reliance on fossil fuels is gradually increasing. Continuous consumption of fossil fuel has direct impact on environment [1]. Renewable energy technology is clean and environment friendly. Biomass is one of the most abundant and potential resources of energy around the world. Biomass energy is defined as the utilization of organic materials to create energy. Biomass can be converted to biofuel including bio-oil and biogas [2-3]. Bio-oil is produced from multiple types of feedstock, such as palm kernel shells, karanja seeds, wood sawdust, sewage sludge, sugarcane etc. where the properties of bio-oil depend on feedstock characteristics and parameters of pyrolysis Bio oil comprises a complex mixture of over 300 organic materials from aldehydes, esters, ketones, acids, alcohols and oligomers obtained from lignin. Such chemical compositions in the oils offer significant characteristics to bio-oil production, which differs from conventional oils obtained from petroleum. Some of the properties can lead to undesirable results, especially for certain applications like oil. The existence of these unfavourable properties has a negative impact that restricts bio-oil use in multiple applications. Some of the physical properties are the content of oxygen and water, viscosity, corrosively, and ultimately the behaviour of combustion [4]. About 35-40% of oxygen present in the pyrolysis oil reduces the energy densities of the oil which is directly connected to the heating value [5]. Water content in the oils has resulted in the feedstock's original moisture due to a dehydration reaction that occurred during the pyrolysis process ranging from 15% to 30%. The presence of water in bio oils lower the heating value and in the same time causes greater ignition delay which decreases the combustion rate especially in the engine [6]. However, the positive effects of water to reduce oil viscosity and leads uniform temperature profile as well as reducing the emission of nitrogen to the air. Czernik and Bridgewater [5] explained that although the oils are free flowing, its viscosity increases with time especially when it is handled at higher temperature. Reactive components in pyrolysis oil such as aldehydes, phenols and ketones are subjected to secondary condensation and polymerization, leading to higher and higher viscosity levels. Bio oils have acidic properties which could cause corrosion on materials

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such as carbon steel and aluminium. At high temperatures, corrosiveness can get severe and increase the water content. High acidity can lead to very unstable bio oil. The pH quality for bio-oil varies from 2-3 and is the product of significant organic acids, mainly acetic acids and formic acids present in the feedstock. Bio oil has a higher efficiency energy production compared to conventional biomass fuels, especially for heat and power generation. It is also viewed as carbon dioxide (CO₂) neutral due to lower sulfur and nitrogen gas content which can lead to lower greenhouse gas emissions [5]. Due to growing in multiple types of biomass globally, great interest of research is among different kinds of biomass as renewable energy resources that provide many opportunities for bio-oil conversion for heat and power generation.

Palm kernel shell (PKS) is one of the by-products produced from the palm oil milling operation but however is rapidly becoming an important supply of feedstock for biomass energy generation. Although always traditionally used by palm oil mills as a source of energy, pastime from power generators is growing. Given its excessive energy content (14-20GJ/t) and the reality that it is a waste product. In ASEAN countries such as Thailand, Malaysia and Indonesia, the rapid development of palm oil industries leads to the abundance of these biomass sources increasing. PKS is the shell fractions left after the nut has been eliminated and one of the fibrous materials. Large and small shell fractions had been mixed with dust-like fractions and small fibres. By comparing PKS with other biomass sources, the moisture content in the kernel shells is low suggesting values between 11% and 13%. The rapid hydrothermal process is one of the ways to transform biomass into bioenergy. Microwave approach provides instantaneous heat and quick heating to convert agricultural waste into a product with added value. Salema & Ani, 2011 [7] reported that conventional heating methods has a lot of drawbacks compared to microwave pyrolysis. Hydrothermal liquefaction process undergoes thermochemical decomposition in the absence of oxygen to transform biomass with high temperature. Through the hydrothermal process, biomass produces biochar, volatile and bio-gas. During hydrothermal liquefaction process, three types of reaction named drying, primary reaction and secondary reaction occur. Hydrothermal liquefaction process processing provides the atmosphere with greater efficiencies and less pollution. Hydrothermal process is complex where biomass undergo many stages of decomposition which result various change in specific volume [8]. The concept of integrated bio-refinery is the unparalleled solution which comprise the generation of hydrocarbon grade fuels at a time with valuable products from the pyrolysis derived bio-oil [9]. Many types of pyrolysis are practiced based on different condition. One of the modern pyrolysis techniques is the microwave assisted pyrolysis.

Microwave-assisted pyrolysis (MAP) is one of the current technologies emerging as one of many ways to turn biomass into high-quality and high market value products due to its emergence. It has become one of the hot topics among researcher that offers vast advantages compared to conventional pyrolysis that uses traditional electrical heating method [10]. Problems such as slow heating and the need to minimize particle size in order to increase the heating speed can be solved by microwave pyrolysis. Microwave pyrolysis can also help greatly to save energy and increasing the processing time of biomass production while at the same time improving the quality of bio char, bio gas and bio oil. Microwave pyrolysis and bioenergy include the conversion of oil palm, wood, microalgae, corn stover and sewage sludge [11]. Feedstocks do not need pre-treatment processes in microwave-assisted pyrolysis such as drying and grinding as feedstock heating can be driven through this technique. The moisture content that exists in the feedstock act as an adsorption material especially for irradiation as it can initiate the pyrolysis process [12]. In addition, decrease in feedstock size is always necessary when using conventional pyrolysis as contrast to microwave-assisted pyrolysis which can use feedstock's original size. Zhang et al. 2017 [11] stated that conventional pyrolysis is highly dependent with the particle size of the feedstock as larger particle size produces low thermal conductivity and heat transfer thus creates a negative impact on the efficiency of bio-oil production. Having the ability to increase the overall heat transfer and high yield of pyrolysis materials, tiny particles in conventional pyrolysis are always favourites given the lengthy pre-treatment process involving testing of biomass feedstock, elimination of moisture and reduction of size. Microwave-assisted pyrolysis using microwave radiation as a heat source to transform electromagnetic energy to heat energy. Heat can be generated in microwave-assisted pyrolysis due to the ability of the microwave that can penetrate through the feedstock thus providing energy without the need of using external source of energy [13]. The heat interaction would create a temperature gradient that occurred because of the feedstock's poor thermal conductivity, thereby spreading the volatile material from the inside to the outside surface from the higher temperature region to the lower temperature region. Using microwave radiation can ensure uniform heat distribution, high heating efficiency with better heat transfer, rapid internal heating and speed up bio-oil production. Microwave-assisted pyrolysis shows about 90 percent of the operating efficiency in terms of converting electricity into thermal energy and providing high-powered heat source. Microwave-assisted pyrolysis offers more reliable process and are less costly in comparison to conventional heating method [14]. During the pyrolysis process, high heating rates and pyrolysis temperature can always be reached as well as shorter residence time if microwave absorbents are mixed with feedstock for biomass. This is due to the ability of microwave absorbents to absorb the microwave energy and conveyed it to the poor absorbing material [15]. Although microwave absorbents are great material that would help in increasing the pyrolysis end product especially bio-oil, however, the possibility for the volatile matter to enter secondary reactions where the vapour would break down into non-condensable gases are high due to sudden elevated temperature during the process which could reduce the yielding of bio-oil [11]. Zhang et al. 2017 [11] stated that there are few methods that can be used in mixing the feedstock with microwave absorbent. The first approach is to mix the absorbent microwave with feedstock of biomass before starting the microwave-

assisted pyrolysis because non-uniform mixing might occur throughout the pyrolysis process as both the microwave absorbent and feedstock have different bulk density and also the feedstock of the smaller particles would drop and remain at the bottom of the mixing plate. In order to improve heat transfer, the absorbent bed agitation is required as it facilitates uniform mixing between the absorbent surface of the microwave and the feedstock of biomass.

Catalyst may be used to boost microwave pyrolysis bio-oil yield. Catalytic pyrolysis has been studied to improve the quality of pyrolysis liquid and decrease yield of non-condensable gases [16]. Catalyst reaction such as metals (Al or Cu), metal oxides (CaO, MgO, HZSM-5, etc.), metal salts (NaCl, KCl, NaOH, etc.) and acids can be used for bio-oil production in microwave pyrolysis. Usually, microwave-assisted pyrolysis reaction catalysts are metals (Al, Fe, Cu), metal oxides (CaO, MgO and Fe₂O₃), metal salts and acids (H₂SO₄). Catalytic microwave-assisted pyrolysis offers a number of benefits over normal microwave-assisted pyrolysis in terms of pyrolysis performance and efficiency. Bio oil produced from fast pyrolysis must not contain any oxygen, hence the use of catalyst throughout the process of pyrolysis. Catalysts effectively remove oxygen from the feedstock of biomass and thus improve the properties of the bio-oil itself. There approaches when utilize the usage of the catalysts namely catalytic cracking and hydro treating (Liu et al., 2014) [6]. To counter these undesirable properties obtained, the process has been modified to fully utilize the used catalyst properties that can be separated into two processes that are both in-situ and ex-situ. In-situ catalytic process involves combining catalysts as well as feedstock in the reactor together. Ex-situ catalytic process involves separation of catalyst from the feedstock before being placed onto the secondary reactor generally known as catalytic bed at which the primary pyrolytic vapours pass through it [17].

There are many factors that effect on pyrolysis of biomass feedstock. The yield of the pyrolysis product mainly depends on the characteristic of the biomass feedstock and the procedure parameters of temperature, microwave power, pyrolysis time, biomass feedstock characteristic etc. Temperature can have a major impact on the biomass feedstock pyrolysis. Temperature influence on bio oil distribution pyrolysis from 500°C to 800°C [18]. Nonetheless, the use of microwave-assisted pyrolysis is to ensure that the feedstock of biomass undergoes decomposition at lower temperature faster in order to achieve maximum bio-oil yield compared to conventional heating process. Nevertheless, different heating temperatures during microwave-assisted pyrolysis can affect the characteristics of bio-oil [19]. Xie et al. 2014 [20] studied that at temperature between 450°C to 650°C was experimented to determine the percentage of bio-oil yield. The yield of bio char decreased and the yield of biogas increased as the temperature rose. The temperature increase has also resulted in a high yield of pyrolysis oil and the maximum yield of pyrolysis is around 550°C. The increase in the yield of pyrolysis oil is due to solid devolatilization, depolymerisation, and decarboxylation, which has been promoted by high temperatures since more energy has been involved in chemical reactions. The energy increase may break the strong organic bonds as well as release more volatiles to create condensable gas. That is also the reason why bio char decreases and biogas temperature increases. The reduction in bio-oil yield, however, occurs after 550°C.

This is due to the process of secondary pyrolysis once the temperature reaches 550°C. Too high temperature undergoes a secondary stage of pyrolysis that makes condensable volatile convert to non-condensable gasses and decreases pyrolysis oil yield when the temperature of the pyrolysis reaches 550°C [21]. Microwave power is used to adjust the microwave-pyrolysis process temperature. Increased microwave power level and increased cavity microwave density, resulting in increased microwave energy absorption by biomass feedstock. The increased microwave energy absorption of biomass feedstock creates a stronger interaction between biomass feedstock and microwave field. Song et al. 2017 [22] mentioned that the changes of microwave power level on tire powder using microwave pyrolysis can affect bio oil yield. The result showed that the yield of pyrolysis liquid increased and that high microwave power was attributed to a high temperature of pyrolysis that could produce more liquid pyrolysis. The pyrolysis time for bio-oil production is included in the microwave pyrolysis parameter. It is the contact time between the feedstock of biomass and the region of microwave. The time of pyrolysis is described as the time between the feedstock of biomass starts to decompose and the pyrolysis process is completed. Once starting to heat biomass feedstock inside the microwave oven, the time required to achieve the desired temperature of pyrolysis starting from the original time. The difference between the time of pyrolysis and the required time of pyrolysis is called the time of residence. Residence time is important because it shows the actual time of pyrolysis in the biomass feedstock microwave pyrolysis. Low yield of coal, lower yield of pyrolysis oil and low yield of bio char develop at longer times of residence. Wang et al. 2015 [23] studied that utilize calluna vulgaris in microwave pyrolysis to determine bio oil yield at various pyrolysis times. If the time of pyrolysis increases from 1 to 10 minutes, the production of pyrolysis oil increases. It is because longer pyrolysis time can be produced to ensure that biomass raw materials undergo maximum pyrolysis process and high volatility. In fact, if residence time increases more, the yield of bio-oil decreases. Because of the residence time increases more; the temperature becomes too high, resulting in condensable vapours being exposed to secondary reactions to form non-condensable gas. For microwave pyrolysis, an optimal residence time must be set, but the optimum residence time must be various by the other parameters. Microwave pyrolysis is characteristic of biomass feedstock. Moisture content in raw materials from biomass can act as an absorbent microwave because water can act as high absorbents of microwaves. Increasing the moisture content also led to high bio-oil yields as microwave absorption of biomass feedstock increased. However, for microwave heating, high moisture content of biomass feedstock is not a fine parameter. Throughout microwave heating, the biomass feedstock temperature will increase, and the moisture content would evaporate. Loss of moisture content can impact raw materials from biomass, resulting in lower microwave absorption and lower heating levels. Higher moisture content

can result in high tangent value in the feedstock of biomass. Although the content of moisture in biomass raw materials can improve the process of microwave pyrolysis and maximize the production of bio-oil, the bio-oil is diluted due to high content of moisture in pyrolysis oil [24].

The main aim of this research is to analysis the effect of different parameters to extract bio-oils from palm kernel shell, to compare the yield of bio-oil produced and to characterize the bio-oil production by using microwave-assisted rapid hydrothermal liquefaction and conventional heating processes.

2. MATERIALS AND METHODOLOGY

2.1 Experimental setup

2.1.1 Biomass Feedstock

In this experimental work, the agricultural waste from palm farms, PKS, was used as biomass feedstock which is widely found in Malaysia and neighbouring regions. The PKS samples were collected from Ensengei Palm Oil Mill, Samarahan, Sarawak, Malaysia. Firstly, to remove the moisture content, the PKS samples were dried in a oven (Panasonic NN-ST342M) for 2 hr at 105 °C and then crushed to a smaller size of particle sizes around 212–300 μm, 300–600 μm, 600μm–1, 18 mm, and 1, 18–2, 36 mm by using a crusher (Kenwood multifunction). PKS has a high density of energy and solid biofuel of high grade. High calorific value, low sulfur content, excellent year-round availability, simple handling and crushing, minimal biological activity due to the low moisture content and no variety in species are features of PKS.

2.1.2 Microwave Assisted Rapid Hydrothermal Liquefaction Process

Schematic of microwave-assisted experimental set up for pyrolysis was shown in Figure.1(a). A Panasonic NN-ST342M microwave oven (max. power of 800W and frequency of 2450MHz) was modified to allow the drying and pyrolyzing the agricultural waste. At the top-centre of the microwave oven a hole of 40 mm diameter was made. A quartz reactor with tube size of 40 mm diameter, height of 250 mm and the socket size of C24/29 was mounted on the microwave oven and supported using a retort stand. A thermocouple (EXTECH, USA) was employed for measuring the sample temperature. A T-shaped connector with C24/29 socket was used to link the quartz reactor gas outlet to the Liebig condenser fitted with water cooling system. The other end of the Liebig condenser was connected by L-shaped connector with C24/29 to 3 necks collecting flask. The experiment was conducted by placing samples of small particles in the quartz reactor and then put inside the microwave oven. Standard procedures and safety precautions were adopted to prevent leakage of microwave radiation to the surroundings Figure 1(b) shows the modified microwave-assisted experimental set up for hydrothermal liquefaction process in the lab.

2.1.3 Conventional Heating Pyrolysis

The schematic and set-up for conventional heating pyrolysis was shown in Figure 2 (a & b). A 250ml round bottom borosilicate-glass flask was mounted on a 360W heating mantle and was attached to a T-shaped connector. To check the temperature inside the flask, a thermocouple with multimeter (digital, EXTECH, USA) was inserted at the top of the T-shaped connector. Further, a Liebig condenser was connected to a T-shaped connector. The Liebig condenser outlet is connected to an L-shaped connector and a collecting flask as well. Similarly, to the modified microwave, the gas vapor which flows from the flask to the Liebig condenser is condensed using a water-cooling system. The collecting flask collects oil settle from the condenser and its weight was measured and recorded.

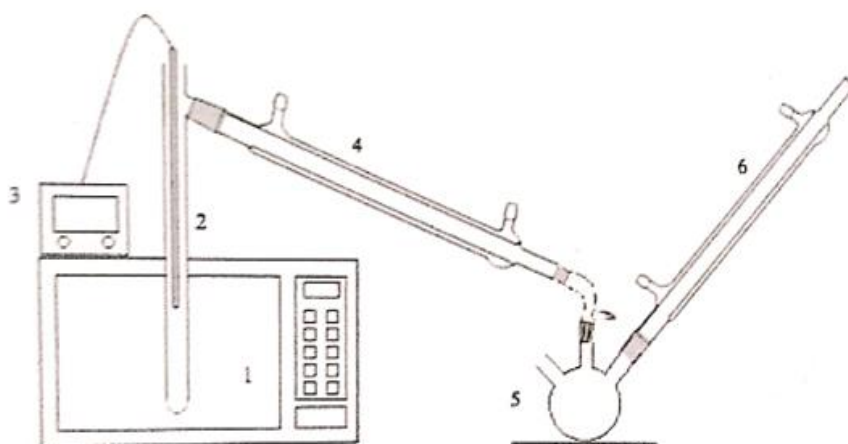


Figure 1(a): Schematic of modified microwave-assisted experimental set up for hydrothermal liquefaction process. (1) Microwave oven, (2) Quartz reactor, (3) Digital Multimeter and thermocouple, (4&6) Liebig condenser (5) Necks collecting flask.



Figure 1(b): Modified microwave-assisted experimental set up for hydrothermal liquefaction process

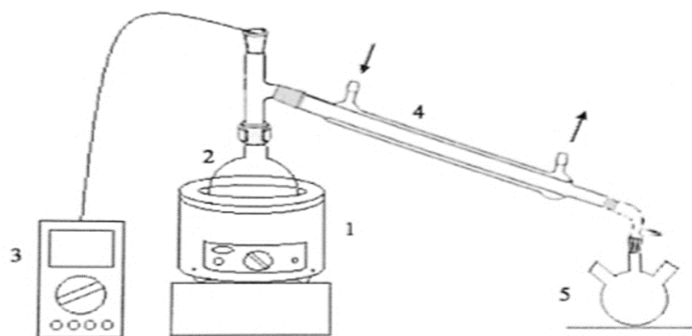


Figure 2(a): Schematic of conventional heating hydrothermal liquefaction process experimental set-up. (1) Heating mantle, (2) Round bottom flask, (3) Digital multimeter and thermocouple, (4) Liebig condenser, (5) Three necks collecting flask

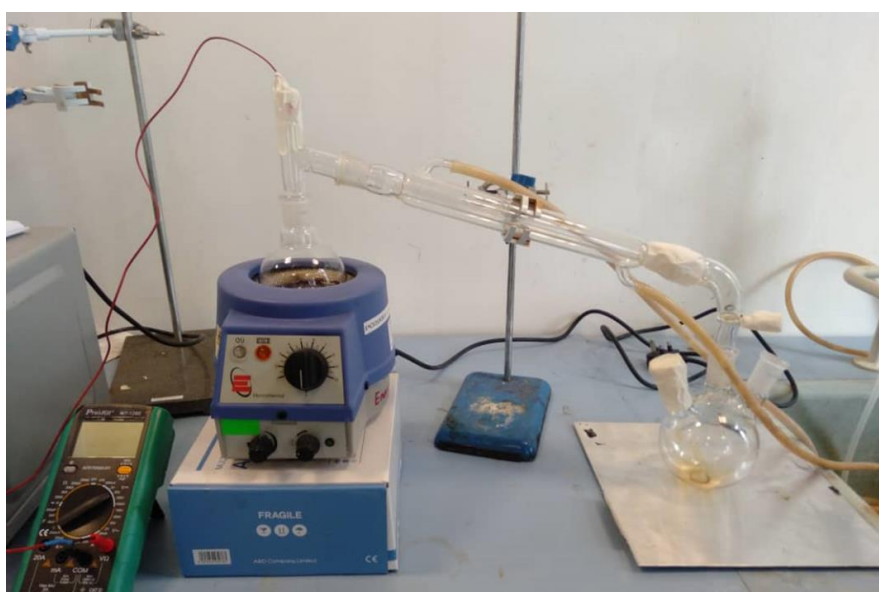


Figure 2(b): Experimental set-up of conventional heating hydrothermal liquefaction process

2.1.4 Microwave Assisted Rapid Hydrothermal Liquefaction Process

The sample of agricultural waste was sewed meshed into a small particles and feed into the quartz reactor. To avoid gas leakage during the pyrolysis process, all holes of equipment was covered by aluminium foil. The experiment was conducted by inserting 20 grams of PKS samples in a quartz reactor and inserting them in a modified microwave oven. The optimal microwave oven power level for this experiment is 800 W. The experiment was repeated thrice for three pyrolysis process time 6 min, 9 min and 12 min. The bio oil was collected in a three-neck collecting flask from the volatile substance produced and equipment was washed with dichloromethane. While the carbonaceous residue (char) was directly obtained from the quartz reactor. The yield of bio-char and bio-oil were measured by their weight and the yield of gas was calculated by weight difference.

2.1.5 Conventional Heating Process

20 gr of PKS sample feedstock was fed into the 250ml round bottom flask and kept on top of the heating mantle. Digital multimeter thermocouple was connected from top to the T-shaped connector and properly sealed to measure the temperature inside the flask. The heating mantle was then set to a maximum level of 10 and can be adjusted according to the desired temperature. In this work Temperature for conventional pyrolysis was set at 350°C, 400°C, and 450°C meanwhile the conventional pyrolysis time was set at 30 min, 40 min and 50 min for each of the temperature. Volatile substances were collected and condensed in the collecting flask and yielded bio oil weight was measured.

2.1.6 Yield calculation of Bio Oil, Bio Char and Bio Gas

The mass of PKS feedstock samples was measured before starting of the experiment, while the mass of the bio oil yielded at the end. The following Eq. (1) - (3) [25-27] were adopted to calculate yield of Bio Oil, Bio Char and Bio Gas.

Bio-oil yield:

$$Y_{\text{bio-oil}} = m_{\text{bio-oil}}/m_{\text{sample}} \times 100\% \quad (1)$$

Where,

$m_{\text{bio-oil}}$ = mass of the bio-oil produced after pyrolysis process

m_{sample} = mass of the biomass feedstock before starting of pyrolysis process

Bio char yield:

$$Y_{\text{bio char}} = m_{\text{bio char}}/m_{\text{sample}} \times 100\% \quad (2)$$

Where,

$m_{\text{bio char}}$ = mass of the bio char obtained from pyrolysis process

m_{sample} = mass of the biomass feedstock before starting of pyrolysis process

Bio gas yield:

$$Y_{\text{bio gas}} = 100\% - Y_{\text{bio-oil}} - Y_{\text{bio char}} \quad (3)$$

2.1.7 Characterization of Bio Oil properties:

The Bio Oil samples obtained from both microwave-assisted and conventional heating methods were analysed to determine their properties. Fourier Transform Infrared Spectroscopy (SHIMADZU, IRAFFINITY-1) was employed to analyse the bio-oil functional groups over a 4000 to 500 cm^{-1} region. The calorific value of the produced bio-oil was determined using a Bomb Calorimeter (Parr 6400). pH value of the bio-oil was measured by a pH meter (Star121, Orion). The energy properties of Bio Oil were determined by measuring bio-oil's heating value through higher heating value (HHV) and lower heating value (LHV) as well. A bomb calorimeter was used measure HHV. Heat that is removed during the process of combustion in a condensed state is referred as HHV, whereas LHV is related to the combustion that is based on gaseous water as the product [28]. Multiple ways exist to calculate the value of HHV and most of them depend on the composition of C, H, N and S. Basically, on how these four composition oxidise into their respective products during combustion process whereas the other correlations mainly assuming that the HHV of bio-oil is directly proportional to oxygen since combustion requires oxygen to ensure complete process [29]. HHV value was calculated following the Eq. (4), (5) and (6).

$$\text{HHV} = 0.3491\eta_c + 1.1783\eta_H + 0.1005\eta_S - 0.1034\eta_O - 0.0151\eta_N - 0.0211\eta_{\text{ash}} \quad (4)$$

$$\text{HHV} = 0.3382\eta_c + 1.4428(\eta_H - 0.125\eta_O) \quad (5)$$

$$\text{HHV} = \text{LHV} + 21.978 \eta_H \quad (6)$$

Where:

HHV = High Heating Value of bio-oil (MJ/kg)

LHV = Low Heating Value of bio-oil (MJ/kg)

η_c = Weight percentage of carbon content of bio-oil (%).

η_H = Weight percentage of hydrogen content of bio-oil (%).

η_O = Weight percentage of oxygen content of bio-oil (%).

η_N = Weight percentage of nitrogen content of bio-oil (%).

η_{ash} = Weight percentage of ash of bio-oil (%).

3 RESULTS AND DISCUSSIONS

Impact of hydrothermal process time and temperature on Bio Oil yield were analysed and illustrated.

3.1 Physical Appearance Bio-oil

The bio-oil was extracted from PKS by using microwave-assisted hydrothermal liquefaction process and conventional heating. In microwave assisted hydrothermal experiments were conducted at 350°C and 450°C for a period of 6 minutes, 9 minutes, and 12 minutes. While in conventional heating process, 350°C, 400°C and 450°C with pyrolysis time of 30 minutes, 40 minutes and 50 minutes respectively. The bio-oil obtained from both of the conversion method is in light orange colour and bio-char are in black colour. Figure 3 shows sample of bio-char and bio-oil obtained from experiment.



Figure 3: Samples of bio-char and bio-oil obtained from experiment

3.2 Yield of Different Fraction

20 grams samples of Palm Kernel Shells (PKS) have been used for all the process to occur for each run of the experiment. Each of the following discussion will be based on the yield of the product obtained from 20g of the Palm Kernel Shell (PKS) and based on their respective methods. Palm Kernel Shell's total product yield is described and presented in Tables 2 and 3. Biogas results was a very challenging task to be collected and calculated due to the difficulty to capture the vapour during conversion, so the percentage yield of biogas was determined by the difference of 100 percent with the amount of both bio-oil yield and bio char. While others, it was measured directly in the case of the bio-oil and bio char, as the quantity of raw material is kept constant. Apart from that, Figure 4 and Figure 5 displayed the analysis of the difference fraction performed through microwave-assisted and conventional heating for the product yield.

3.3 Hydrothermal under Microwave Heating Assistance

The percentage yields of bio-oil from Palm Kernel Shells are presented in Table 1 and Figure 4. Table 1 displays the results collected and measured to calculate the yield of bio-oil at 350°C and 450°C while pyrolyzing the Palm Kernel Shells under microwave heating assistance. The highest percentage yield for bio-oil is 25.60 wt% at 9 minutes with temperature 450°C while the lowest recorded bio-oil yield is around 10.70 wt% during 6 minutes with temperature 350°C. And the other by-product formed through hydrothermal is bio char, which is the carbonaceous residue and biogas as well. Each of these products showed a maximum yield of 49.35 wt% and 54.65wt% within 6 and 9 minutes, respectively, at the same temperature of 350°C. And it is clear in Figure-4 that the yield for bio-oil slowly increased with an increase in pyrolysis temperature. When pyrolysis temperature is 350°C, the yield ranged from 10.70 wt% to 21.30 wt%, while the yield was 17.65 wt% to 25.60 wt% during hydrothermal temperature 450°C. Both temperatures show the highest percentage yield when the raw materials undergo 9 minutes of hydrothermal time, indicating that both temperatures have reached an optimum value at 9 minutes. However, yield dropped after the period goes beyond 9 minutes. This proves that the microwave-assisted pyrolysis needs specific times and temperatures to achieve an optimal bio-oil yield. Microwave-assisted pyrolysis at that same temperature of 450°C recorded the highest bio-oil yield for 25.60 wt% and yielded lower bio-char.

Table 1: Product yield of Palm Kernel Shells at different pyrolysis time and temperature using microwave-assisted hydrothermal liquefaction process.

Temperature (°C)	Time (min)	Bio-oil (wt%)	Bio-char (wt%)	Bio-gas (wt%)
350	6	10.70	49.35	39.95
	9	21.30	24.05	54.65
	12	16.30	29.55	54.15
450	6	23.81	27.62	48.57
	9	25.60	25.12	49.28
	12	17.65	33.45	48.90

3.4 Conversion under Conventional Heating

This experiment involving conventional heating pyrolysis, a modified conventional heating method in research methodology is being used to extract bio-oil from palm kernel shells. After that, the yields of the bio-oil and by-product such as bio-char and bio-gas are being calculated. All 3 different yields from palm kernel shells through conventional heating process are tabulated and presented in Table 1 at pyrolysis temperatures of 350°C, 400°C as well as 450°C. Figure 5 shows the total product yield obtained via conventional heating pyrolysis. The yields of bio-oil ranged from 11.13 wt% to 36.07 wt%, referring to Table 1. It's also observed that the highest bio-oil yield resulted at 400°C instead of 450°C as the percentage decreases to a range of 11.13 wt% -13.03 wt%. Violent reaction to thermal decomposition takes place at a higher temperature which could induce secondary pyrolysis that yielded more biogas than bio-oil. Presented in Figure 5, result generated and demonstrated here that product yield for bio-oil kept increasing as the temperature and time also increased, but there was a slightly decrease in the bio-oil yield as the pyrolysis temperature exceeded 450°C while the yield for bio-char and bio-gas increased marginally with inconsistencies. It's recorded that maximum bio char and biogas was 63.97 wt% and 50.45 wt% respectively. On the basis of the tabulated data and the graph, it can be obviously found that the highest bio-oil yield from the palm kernel shell can be obtained when the pyrolysis temperature is 400°C and the pyrolysis time is 40 minutes, as it yields 36.07 wt% of bio-oil. In addition, the yield of the bio-char as well as bio-gas is also low at this pyrolysis temperature, for only 40.62 wt% and 23.31 wt% respectively.

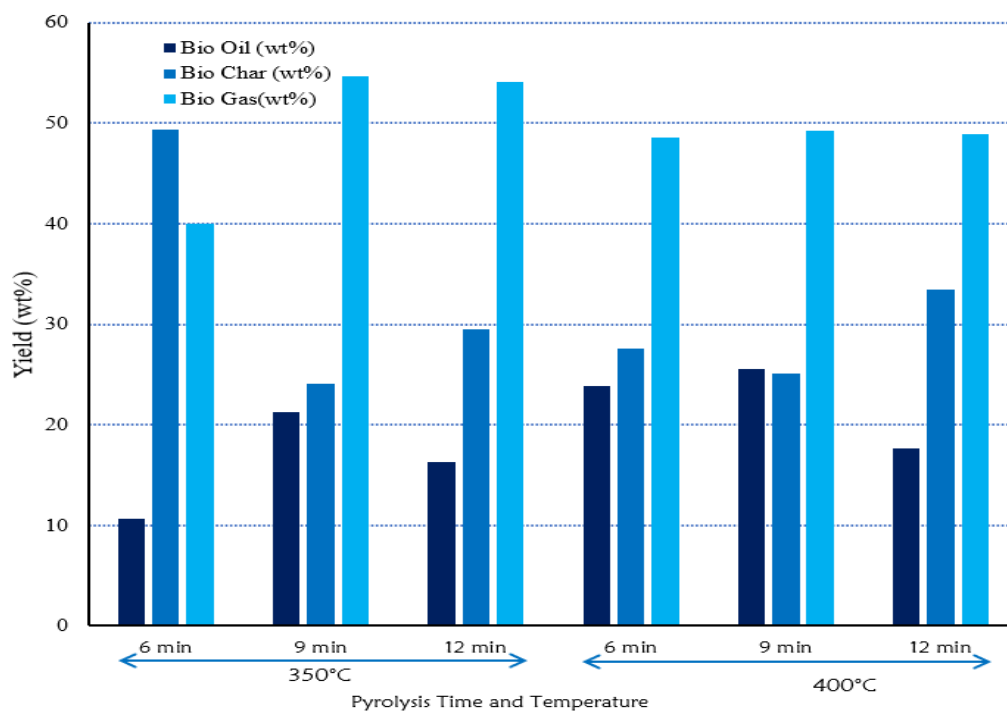
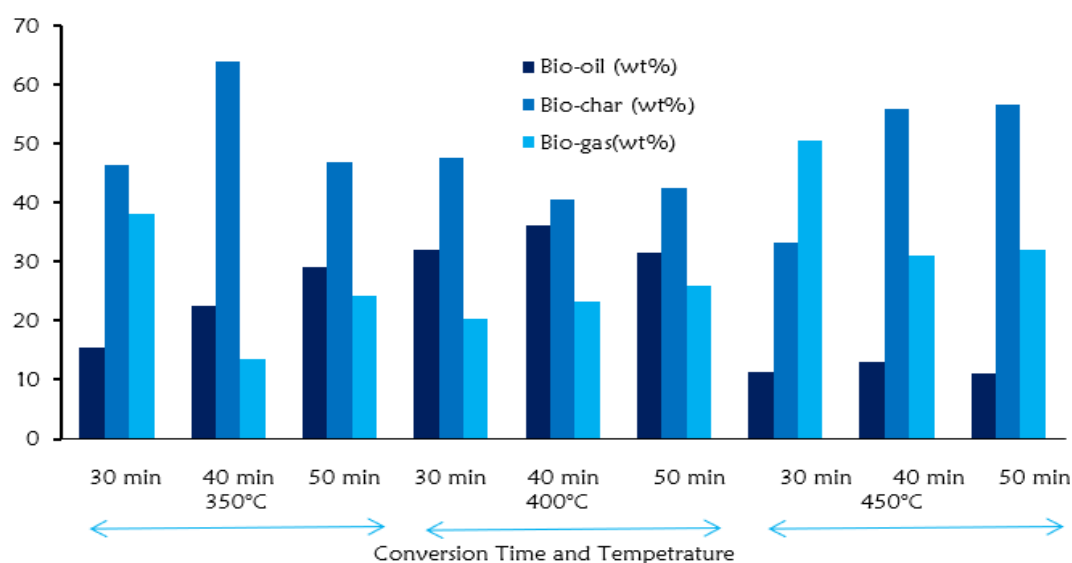
**Figure 4:** Overall product yield of microwave-assisted pyrolysis

Table 2: Product yield of Palm Kernel Shell at different pyrolysis time and temperature using conventional heating.

Temperature (°C)	Time (min)	Bio-oil (wt%)	Bio-char (wt%)	Bio-gas (wt%)
350	30	15.42	46.48	38.1
	40	22.47	63.97	13.56
	50	29.01	46.8	24.19
400	30	32.09	47.67	20.24
	40	36.07	40.62	23.31
	50	31.48	42.5	26.02
450	30	11.27	33.28	50.45
	40	13.03	55.83	31.14
	50	11.13	56.72	32.15

**Figure 5:** Overall product yield of conventional heating process

3.5 Factors Affect Different Conversion

There have been various key parameters that need to be understood in order to obtain optimum conversion of PK into bio-oil. Therefore, the two conversion methods used in this research are being evaluated and analysed using various types of parameters simultaneously to determine the efficiency and optimum parameters for extracting bio-oil from the palm kernel shells. Different parameters are chosen being used for each experiment and the impact of such parameters will then be discussed in detail towards the yield of the product. Factors which affect the method of conversion are a) Conversion temperature and b) Conversion time.

3.5.1 Effect of Conversion Temperature

The temperature of conversion is one of the significant parameters that impact bio-oil production. For the biomass feedstock it needed the optimum temperature to decompose and generate its by-product. The experiment was performed at 350°C and 450°C respectively, and its objective is to investigate the bio-oil yields obtained from microwave-assisted pyrolysis at different pyrolysis temperatures. Based on Figure 6, it could be seen that once the temperature of conversion increased from 350°C to 450°C, the yield of bio-oil increased from 10.70 wt% to 25.60 wt%. Apart from that, as the temperature rose to 450°C, a gradual decrease in the yield of the bio char was recorded, while the yield of bio gas slowly increased with high temperatures but was still below the acceptable yield. The experiment proves that the minor decreases in the product yield of bio-char, and it can also be obviously indicated from the graph that bio-gas yield increases due to secondary reactions that favoured the generation of non-condensable gas than bio-oil when temperature rises. This condition was confirmed as Zhang et al. 2017 [11] reported that carbon dioxide and water content were in an endothermic reaction, thus enhancing the conversion of condensable vapours to non-condensable gasses during second reactions at higher pyrolysis temperature.

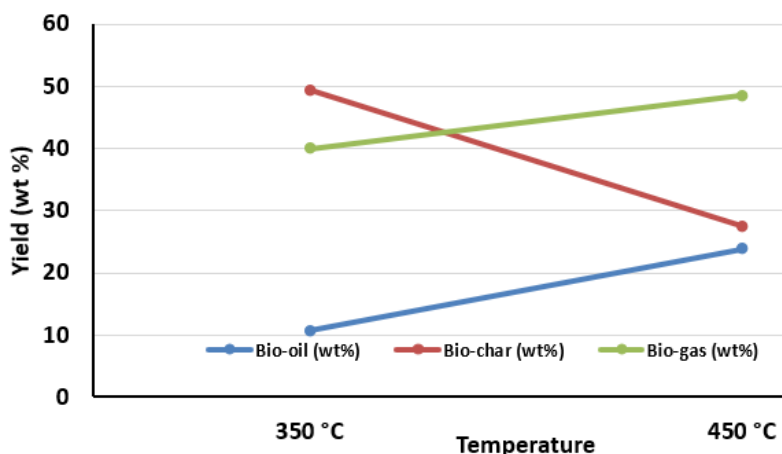


Figure 6: Bio-oil yield for microwave-assisted hydrothermal in different temperature

Throughout this study, it can be found that it produces maximum bio-oil when the temperature is at 450°C that implies it is within the range of optimum conversion temperature (300°C - 600°C). Nevertheless, the yield of bio-oil decreases after the optimum temperature has been reached, which indicates that the pyrolysis is affected by temperature. Microwave-assisted hydrothermal provides quite consistent thermal distributions, since microwave heating is the energy transfer rather than transfer of heat. During microwave-assisted hydrothermal, the microwave transmitted further into particle of the feedstock and this energy, which is radiated from the microwave, is converted into heat, thereby producing a temperature gradient from the inside to the outside. Then the area surrounding is lower than inside of the feedstock particle as heat is continuously stored inside the feedstock until it is transferred to the outside part of the particle. So, mainly as a result of heat loss here on particle surface, the feedstock can decompose and release volatile substances at lower pyrolysis temperature area. Referring to Figure 6, it illustrates the results of bio-oil yield for conventional heating process in different temperature. It demonstrates similar patterns in conventional heating process, as well as in the microwave-assisted hydrothermal.

The production of Palm Kernel Shell pyrolysis product (PKS) from different temperatures can be seen in Figure 6. As referring to the Figure 6, the yield of bio-oil increases as the temperature rises, but it shows a sharp decrease in yield at 450°C. The yield of bio char and biogas display a similar characteristic once the temperature rises from 350°C to 450°C, and both of those products decrease when the temperature rises from 350°C to 400°C but when it reaches its peak temperature of 450 °C, the yield rises to 56.72 wt% and 50.45 wt% respectively. Similar with microwave-assisted pyrolysis, it can also be clarified that now the increased yield of bio char and biogas could be due to secondary thermal decomposition, leading to a lower yield of product at 11.13 wt%. Bio-oil production was related to the devolatilization and depolymerization of organic matter where higher temperatures were needed to break their organic bonds, and this is claimed that thermal cracking at higher temperatures became more significant [13].

Through convection, conduction and radiation, the heat transfer occurs from high temperature gas to the surface of the feedstock particle, thereby further transferring the heat energy into the inner core. Because of the low thermal conductivity of the feedstock material during conventional heating, it is therefore possible to transfer volatile matter at a higher temperature region in achieving its desired temperature gradient from inside of the feedstock towards the outside surface.

3.5.2 Effect of Pyrolysis Time

One of the most key parameters for transforming biomass into bio-oil, bio-char and bio-gas is conversion time. To achieve a proper and complete conversion cycle, the interaction between the heating and the biomass feedstock must be controlled. Different heating times were set for each conversion process in this section to determine the optimum product yield it can obtain throughout the time period that has been set. Figure 7 illustrates the product yield of microwave-assisted pyrolysis during the conversion time for each experiment is maintained constant (6, 9, and 12 minutes). Figure 8 has shown the product yield for conventional heating process when the conversion period in each experiment run is 30, 40, and 50 minutes. In both figures we can note that the product yield is a similar trend in the result. As the conversion period increased, the yield of the product as well increased until at some stage. Based on Figure 7, the maximum product yield was observed is during conversion time 9 minutes, which results in a bio-oil yield of 25.60 wt%, but once the microwave heating exceeds 9 minutes, it decreases to 17.65 wt%. The bio char yield increased while the pyrolysis time was 12 minutes (33.45 wt%), but in the case of biogas, it is different to the research results of the bio char since it gives a slightly reduced percentage yield of 48.90 wt% compared to the 9 minutes yield (49.28 wt%). It takes a cycle of pyrolysis to be lengthy enough to allow a complete pyrolysis process and to release more volatiles to form the pyrolysis oil. Since the microwave heating is much more efficient and the maximum temperature can be achieved at a faster rate, the pyrolysis times are generally within 6 to 12 minutes.

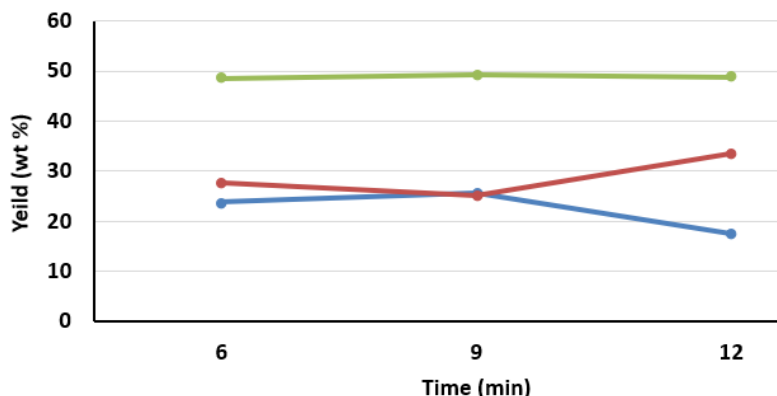


Figure 7: Bio-oil yield for microwave-assisted hydrothermal in different temperature against time

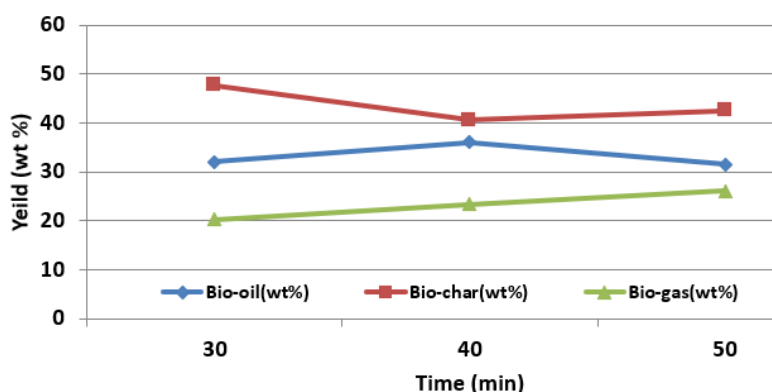


Figure 8: Bio-oil yield for conventional heating process in different temperature against time

Corresponding to Figure 8, it showing the yield of bio-oil for traditional heating process at different times and temperatures. Because conventional heating is an open system, unlike microwave hydrothermal the desired temperature could not be reached in shorter pyrolysis time. It was because the heat loss rate towards the surrounding air is higher than the microwave in an enclosed and regulated device. And so, in conventional heating experiment the pyrolysis time is longer to enable the feedstock to break down into volatile substances. During the pyrolysis time for 400 °C was risen from 30 minutes to 40 minutes, it could be seen obviously that the bio-oil yield increased from 32.09 wt% to 36.07 wt% but decreased to 31.48 wt% once the time was increased to 50 minutes. The decrease in yield was attributed to occurrence of secondary reaction. Non-condensable vapor is generated more than condensable vapour throughout secondary reaction. Then it has shown from the figure that the percentage yield for bio char and biogas is steadily increasing when conversion time increases.

3.6 Product Yield Comparison

Refer to the results obtained in this experiment it can be portrayed that the microwave-assisted hydrothermal offers a benefit over conventional heating. Microwave-assisted hydrothermal can generate more efficient bio-oil in a shorter period of time than conventional heating. It was because microwave-assisted hydrothermal provides rapid heating well to feedstock, which are palm kernel shells, and then at the same time increasing the heat distribution in the feedstock sample, thereby creating more bio-oil in a shorter period of time. Whereas it is found in conventional heating process that it takes longer pyrolysis time to effectively turn PKS into bio-oil. It is not practical to make a direct comparison of the mass percentage yield of each product between the two systems and it is hard to do so because each of these conversion methods has different heating systems. In addition, heat losses to the surrounding environment must also be taken into consideration which can affect the efficiency of the process itself. Nonetheless, a consistent pattern of bio-oil yield generated from both microwave-assisted conversion and conventional heating could be described in terms of the conversion temperature and conversion time.

For both conversion methods, the bio-oil yield increased as the temperature of pyrolysis and the time of pyrolysis rise before optimum temperature and time were reached. For example, in the microwave-assisted hydrothermal experiment, the lowest yield was 10.70 wt% at 6 minutes, during conversion temperature of 350°C. The yield of bio-oil increased to 25.60 wt% when the temperature rises to 450°C with 9-minute pyrolysis time. Since pyrolysis time was beyond 9 minutes, the bio-oil yield declines at both 350°C and 450°C. Same pattern in conventional heating indicates that when the temperature rises from 350°C to 450°C, the bio-oil yield also increases from 15.42 wt to 36.07 wt%. Microwave-assisted hydrothermal is a favoured method because it gives volumetric heating mechanism

for better heating and there is no loss of energy although things were opposed to conventional heating method. The microwave-assisted hydrothermal prevents secondary cracking that could reduce the yield of bio-oil. Conventional heating methods also show the inverse temperature profile by transmitting the heat from the surface to the centre of the material. This particular technique often suffers from some drawbacks due to electric heating, such as heat transfer resistance, heat loss to the surrounding area and damage to the reactor can. Microwave-assisted hydrothermal is also one of the safe and efficient technologies for biomass, which can be used to efficiently extract bio-oil to produce better results.

3.7 Characterization of Bio-oil

The oil collected from microwave and conventional conversion tested to establish and classify the characteristic inhibits of each of the bio-oil samples. Each of the bio oil samples obtained was tested for their calorific value, pH value and functional groups as well. Each test was evaluated using different equipment, such as bomb calorimeter to determine the calorific value of the bio oil. Whereas, pH paper has been used to classify the pH level of the extracted bio oil of both method, and Fourier Transform Spectroscopy (FT-IR) analysis has been carried out to determine and evaluate the composition of functional groups present in the bio-oil.

3.7.1 PH Value

Bio-oil consists of several organic compounds whose chemical composition had led to some important properties defining the bio-oil itself. Since it is a combination of different compounds, the composition of the bio-oil is similar to those of biomass rather than traditional petroleum fuel. It is shown that the pH value of bio-oil is in acidic range 3 and 4 for microwave-assisted and conventional heating respectively. It is reported that the bio-oil from *swietenia macrophylla* (mahogany) wood possesses the PH value of 5.64 [30]. Sutrisno & Hidayat, 2016 [31] reported the pH value of pyrolysis raw bio-oil and upgraded bio-oil are in the range of 2.3–4.4. Bardalai & Mahanta, 2015 [32] found the pH range of 2 to 4 for most bio-oil. And there are few biomasses that give higher pH value to the pyrolysis oil like rice straw, wheat straw etc. Furthermore, several other bio-oils seem to be highly acidic, as the pH value of biomass such as eucalyptus wood is located between 1.8-2.9 [33]. Bio-oil containing low pH values is due generally to the amounts of organic acid such as acetic acids, carboxylic acid and formic acid. When the pH value of bio-oil drops, the bio-oil becomes more acidic, making it more corrosive to products like aluminum and carbon steel as well.

3.7.2 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 Figure 9. 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 (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 [34].

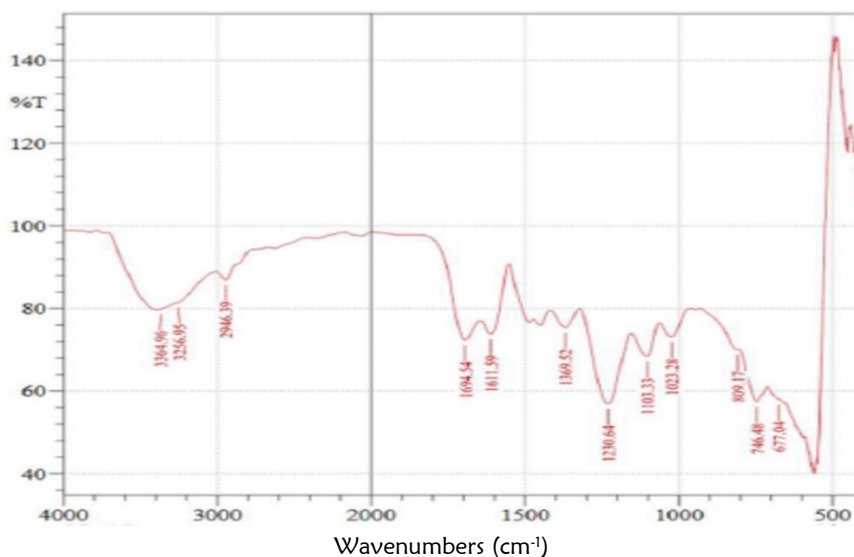


Figure 9: Functional group of Bio-oil for 35g sample at 15 minutes

3.7.3 Calorific Value

Calorific value is the quantity of heat produced during the entire combustion cycle and then when the product was being cooled toward a room temperature of 25 °C. This is also known as fuel combustion heat and is typically measured by using a calorimeter. Bomb calorimeter represents the gross value or high heating value of the oil (HHV) and is expressed in Mega-Joules per kilogram (MJ/kg) whereas the lower heating value (LHV) is the net calorific value and it is obtained from using certain formula and equations. HHV is related to heat that are combusted in a condensed state whereas LHV is the products of combustion that are based on gaseous water and the heat in the vapor is not recovered [28]. The expected calorific values for Palm Kernel Shells (PKS) are tabulated in Table 3.

Table 3: Expected calorific value result of pyrolysis bio-oil at different conversion temperature

Pyrolysis	Temperature (°C)	Calorific Value (MJ/kg)
Microwave-assisted	350	25
	450	26
Conventional heating	350	23
	450	24

Based on the Table 3, the expected calorific value of the pyrolysis oil based on the microwave and conventional method is in range of 24 – 26 MJ/kg which lower than conventional petroleum (40 – 42 MJ/kg). Abdullah et al. 2011 [35] found the calorific value of bio-oil pyrolysis ranging from 20-26 MJ kg⁻¹. Nanda et al. 2014 [36] indicated that the higher heating value of bio oil is achieved at a higher temperature in the shortest possible time. High calorific value in bio oil was due to a small moisture content of the bio oil sample. Composition and ultimate analysis, ash content and calorific value of various biomass feedstock is shown the calorific value for all of the bio-oil from various types of biomass feedstock was in the range of 18.40 MJ/kg – 20.07 MJ/kg [37]. This range is about half or less to the amount of conventional petroleum calorific value. Kawale & Kishore 2019 [38] stated that calorific value of bio-oil produced from a lignocellulosic biomass is evaluated on bomb calorimeter which is 17.093 MJ/kg. Hence, the expected value of calorific value is made by using the results found from previous research and journal. Water content, oxygen content, carbon content, and operating conditions for pyrolysis are among some of the factors that influence the heating efficiency of the bio-oils for pyrolysis. Both the content of water and oxygen has had a negative effect on the calorific value. The higher concentrations of oxygen and water in the bio-oil results in a lower calorific value which reduces the heating value than conventional petroleum fuels. Using both methods with the same 450°C pyrolysis temperature as an example, the predicted caloric value of microwave pyrolysis is much higher. It is due bio-oil pyrolysis in microwaves typically produces much lower oxygen content. Bardalai & Mahanta 2015 [32] stated that oxygen in the bio-oil contributes to increased moisture content, which reduces the amount of hydrocarbon and eventually decreases the heating efficiency. Higher water content decreases the bio-oil's heating value, as it takes evaporation heat during the combustion cycle. Additionally, the amount of carbon content in the feedstock often indirectly influences the bio-oil's calorific value.

4 CONCLUSIONS

Bio-oil from palm kernel shells are extracted by using microwave-assisted and conventional heating process. Based on results, it is found that there is impact of different parameters on the both conversion methods for bio-oil production. The maximum bio-oil collected in microwave-assisted conversion is 25.60 wt % at 450°C temperature, and 9 minutes time. The maximum biochar obtained in these methods is 350°C and 6 minutes with a yield of 49.35 wt%. The maximum is observed for bio-gas at 350°C during the time of 9 minutes with yield of 54.65 wt%. The highest bio-oil yield produced in conventional heating at 400°C in 40 minutes with a yield of 36.07 wt%. The maximum biochar collected at 350 ° C with a period of 30 minutes with a yield of 63.97 wt% and lastly, the highest yield for bio-gas was at 450°C with a yield of 50.45 wt% in 30 minutes. The pH value for bio-oil obtained from palm kernel shells are 3 and 4 for microwave-assisted and conventional heating pyrolysis process respectively. The calorific value ranges of the bio oil are 25 – 26 MJ/kg and 23-24 MJ/kg for microwave-assisted and conventional heating process respectively. 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.

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