MICROWAVE ASSISTED PYROLYSIS OF MORINGA SEED AND KARANJA FOR BIO-OIL PRODUCTION

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Abstract

Microwave-assisted pyrolysis is an alternative technique of conventional heating which undergo thermochemical process to convert biomass to bio oil, biochar and biogas. Microwave-assisted pyrolysis is more rapid and efficient to produce product compared to conventional heating. A modified household microwave oven with 800W was used to pyrolyze Moringa seed and Karanja to become bio oil and biochar. This experiment was repeated in different parameters such as time, temperature and power to obtain maximum bio oil yield. Bio oil yield of Moringa seed increased from 7.2 wt% at 300°C in 5 minutes to 10.6 wt% at 450°C in 13 minutes. Bio oil of both raw materials showed maximum yield when pyrolysis time is 13 minutes in 800W but after 13 minutes, the bio oil yield of Moringa decrease of 2.4% and bio oil yield of Karanja decrease of 4.7%. The calorific value of Moringa bio oil is 25.08MJ/kg whereas Karanja bio oil is 20.36 MJ/kg. Functional group of both bio oil mainly include alcohol, ketones, aldehydes and carboxylic acid. The pH value of Moringa bio oil and 5.86 respectively.

Keywords: Microwave-assisted pyrolysis, bio-oil, biochar, moringa seed, karanja.

1. INTRODUCTION

The continuous consumption of fossil fuels may cause serious issue like risking energy security, increase global climate and risking human health. This situation created strong attraction to search for alternative energy source. Biomass as renewable source that can be converted into bio-oil or biofuel to replace the transportation fuel as it provides environment friendly and economic sustainability. Bio-oil or biofuel derived from biomass via pyrolysis is renewable and carbon neutral suitable to replace petroleum oil and diesel. Moringa oleifera is one of the species of moringa which referred as drumstick tree. It is fast growing and drought-resistance tree which is native from northwestern India but normally cultivated in tropical areas. This plant has made high interest in recent years due to its attributed medicinal properties (Cuellar-Nuñez et al.,2018). Moringa oleifera seed consists of 40% oil and named as "Ben" or "Behen" oil which describe as nutritional seeds. Moringa seeds comprise high content of oleic, behenic and stearic acid and taste bitter (Zhao and Zhang, 2014)., moringa seed act as side product to valorize in integrated bio refinery without affect industrial steam and rich in palmitic, stearic and oleic acid (Martins et al., 2016; Ojiako and Okeke, 2013). Karanja also known as Millettiapinnata is a species of tree in pea family that native to India and

widely distributed along Southeast Asia to West pacific and North Australia. Karanja can grow fast and matures after few years and act as medicinal plant that particularly in Indian medicine for treatment of abscess, skin diseases and ulcers (Bora et al., 2014; Kumar et al., 2012). Karanja oil is reddish brown and it is less toxic and cheaper than jatropha oil (Khayoon et al., 2012; Dewi et al., 2018).

Pyrolysis is defined as thermochemical decomposition of biomass at medium to high temperature in the absence of oxygen from air. The main parameters in pyrolysis process are heating rate, pyrolysis temperature and residence time (Saber et al., 2016). Pyrolysis is complex non-equilibrium process where biomass undergo many stages of decomposition which result various change in specific volume (Nomanbhay et al., 2017). Pyrolysis can be classified into slow pyrolysis, fast pyrolysis and flash pyrolysis. Slow pyrolysis produces large amounts of chars but fast and flash pyrolysis produce high amount of bio oil yield (Kan et al.,2016; Al Arni, 2017). To obtain high liquid production in fast pyrolysis, high heating temperature, short residence time and small particles is needed (Bridgwater, 2012).

Microwave-assisted pyrolysis (MAP) is a new pyrolysis technique that developed in these few years and attracted attention to researchers due to the

advantages over traditional electrical heating method. In conventional heating method, it involved convection and conduction mechanism. Heat transfer from gas to surface of fuel particles via convection and then heat transfer from surface to the inner core via conduction. If the thermal conductivity of materials is low, temperature gradient from outside to inside particles is formed. The direction between heat transfer and mass flow is in opposite direction which led volatile diffuse through higher temperature region (Figure 1) In microwave heating, microwave penetrates the particle and microwave energy convert to heat inside particles. The direction between mass flow and heat transfer is same which led to volatile diffuse from inner core to outside surface via lower temperature region (Figure 1). Microwave pyrolysis is reliabledue to its energy transfer is better, non -contact with feedstock, rapid heating, safe to use (Mushtag et al., 2014; Apodaglio et al., 2016).

Bio oil is a dark brown liquid with free-flowing organic liquid. Bio-oil has also been referred to as pyrolysis oil, pyrolysis liquid, wood liquid, wood oil, liquid smoke and liquid wood (Murray et al., 2014). Bio-oil contains various size molecules derived from depolymerization and fragmentation reactions such as cellulose, hemicellulose and lignin which result in its composition and properties different from fuel oils (Lyu et al., 2015). Bio-oil is considered promising biofuel and can be used as fuel for heat, power or combined heat, act as intermediate feedstock for different chemicals and transportation fuel (Aboulkas et al., 2017). However, bio oil has a high oxygenated and high moisture content but it contains low level of nitrogen and sulfuring compound which cause bio oil thermally instable but reduce greenhouse emissions (Basak and Uzun, 2016). Bio oil has low heating value that cause ignition delay and decrease combustion rate but due to high water content can reduce viscosity of bio oil which led to improve combustion process with good flow characteristic (Basak and Uzun 2016; Bridgwater, 2013). Low pH value of bio oil mainly attributed to amounts of organic acid such as formic acid and acetic acid can led to corrosion wear to construction materials such as carbon steel (Liu et al., 2011). Biochar is stable solid which rich in carbon which show great potential in soil application for improve nutrient retention and enhanced carbon sequestration (Li et al., 2016). Biochar is environmentally friendly and able to bring positive effect on plant growth, soil structure and water management. The formation of biochar contain high carbon content would enhance absorption of microwave energy to form new biochar and consequently higher temperature and increase the pyrolysis progress (Salema and Ani, 2011).

This study is aimed to develop microwave-assisted pyrolysis of biomass for biofuel production. Biomass raw materials such as Moringa seed and Karanja were utilized to convert into bio oil and biochar with microwave assisted pyrolysis technique. Effect of reaction parameters such as heating time, temperature and power were studied in order to optimize the bio oil yield from biomass raw materials. The chemical properties of bio oil obtained from both raw materials was analyzed by Fourier transform infrared (FT-IR) spectro-photographic technique. Energy properties of bio oil obtained from both raw materials was analyzed by bomb calorimeter whereas the pH value of bio oil for both raw materials were analyzed by pH meter.

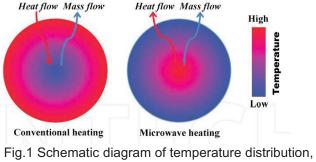


Fig.1 Schematic diagram of temperature distribution, heat transfer and mass transfer in conventional heating and microwave heating (Motasemi et al., 2014).

2. METHODOLOGY 2.1 MATERIALS

The agricultural waste sample selected for this study were Moringa Seed and Karanja. The samples were collected from Faculty of Engineering, UNIMAS. Moringa seed is selected because it contains high nutrients such as oleic acid. Moringa seed is obtained from moringa oleifera also known as drumstick tree. Moringa seed is taken out from Moringa Oleifera and mesh the Moringa seed to become small size particles. Karanja seed is taken out and blend into small particles. The sample of small particles of Moringa seed and Karanja are as shown in Figure 2.



Fig. 2 Small particles of Moringa seed and Karanja respectively

2.2 PRESERVATIVE PROCEDURES

The Moringa seed was dried once a week to prevent loss of oil content inside Moringa seed. The first method to dry the Moringa seed is to put the Moringa seed inside microwave oven and undergo heating with 50°C in 2 hours. The second method is a traditional method that is using sun drying. However, Karanja undergo drying by using microwave with low power and 3 hours to remove the moisture content inside Karanja Seed.

3. MICROWAVE EXPERIMENT SETUP AND PROCEDURE

A household microwave oven with model Panasonic NN-ST342M was modified to let agricultural waste undergo drying and pyrolyzing experiment. A hole with diameter 40 mm was made through the top part of the microwave oven. Quartz reactor is in tube size was placed on top of the center of microwave oven. The quartz reactor was clamped by using retort stand.

The experiment was carried out by placing small particles samples into quartz reactor and followed by placed inside microwave oven. The input microwave power of microwave oven was set to 800W and the microwave frequency was 2450 MHz Thermocouple was used to measure temperature of samples and monitored by digital temperature. Liebig condenser was utilized as cooling medium to condense the volatiles from raw materials during microwave pyrolysis. Safety precaution need to consider as microwave radiation leakage occurs after dig a hole on top of microwave oven. Hence, the hole needs to seal up properly to prevent microwave radiation leakage to surrounding during microwave pyrolysis. The schematic diagram of microwave pyrolysis of moringa seed is shown in Figure 3.

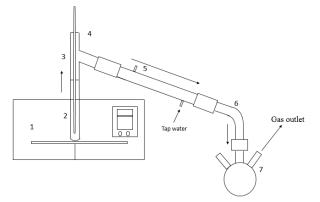


Fig. 3 Schematic diagram of microwave pyrolysis of moringa seed. 1-Microwave oven, 2-Quartz reactor, 3-

Thermocouple, 4-T shape connector, 5-Liebig condenser, 6-L shape connector, 7-3 necks collecting flask

The agricultural waste sample was meshed into small particles and feed into quartz reactor. All the holes of equipment are covered by aluminum foil to avoid gas leakage during pyrolysis process. Agricultural waste samples were dried and pyrolyzed using microwave oven. The experiment was carried out by placing 10 grams of samples in quartz reactor and placed into modified microwave oven. The experiment was repeated in different microwave power level and different pyrolysis time such as 5 min, 7 min, 10 min 13 min and 16 min. The volatile was condensed and deposited at three neck collecting flask. All the instrument was washed with dichloromethane when experiment was finished. The aqueous phase was separated from bio oil by using separation funnel and the bio oil was weighed and its yield was determined. The biochar from quartz reactor was weighed to determine the yield and the biogas yield was calculated by determining the weight difference.

Bio oil yield(%) = $\frac{\text{Weight of bio oil}}{\text{Weight of inital feedstock}} \ge 100$ Biochar yield(%) = $\frac{\text{Weight of biochar}}{\text{Weight of inital feedstock}} \ge 100$

Gas yield (%) = 100 - (bio oil yield + biochar yield)

3.1 BIO-OIL CHARECTERIZATION

The bio oil selected for the characterization was that which gave the maximum bio oil yield at the temperature of 450°C. FTIR spectroscopic analysis were performed to determine the distribution of functional groups present in bio oil. The FTIR spectra of the produced bio oil were recorded in the wavelength range of 500 – 4000 cm-1. Parr 6400 Calorimeter was performed to determine the high heating value of both produced bio oil whereas pH meter was utilized to determine the pH value of both produced bio oil.

4. RESULTS AND DISCUSSION

4.1 MICROWAVE PYROLYSIS OF BIOMASS RAW MATERIALS

This experiment was able to convert biochar and bio oil from microwave pyrolysis and repeated by using various type of biomass feedstock such as Moringa seed and Karanja. Each raw materials sample with 10 g was placed in quartz reactor and the following discussion were concentrated on the results obtained for 10 g of raw materials sample.

4.2 TEMPERATURE CHANGES DURING MICROWAVE PYROLYSIS

The samples of Moringa seed and Karanja were pyrolyzed in the 800 W modified microwave oven at different period of time. The changes of temperature during microwave pyrolysis of both raw materials in 800W was measured and the result was showed on Figure 4. Figure 4 shows the temperature changes of samples Moringa seed and Karanja were almost similar to each other. When microwave pyrolysis undergoes after 4 minutes, both samples showed the maximum temperature which at 487°C and 521°C respectively and slightly decreased when longer heating time. The heating rate for Moringa seed and Karanja are 97.40°C/min and 104.2°C/min respectively. The temperature of Karanja has lower temperature compare to Moringa seed but after few minutes the temperature of Karanja increased sharply and higher temperature than Moringa seed. The heating rate for Karanja was higher than Moringa seed because

Karanja has a smaller particle size compared to Moringa seed. Therefore, Karanja absorb microwave radiation more effectively and thus the temperature increases faster during microwave pyrolysis. Small particles of raw materials can lead to high heating rate due to high external surface area (Li, X. et al., 2018).

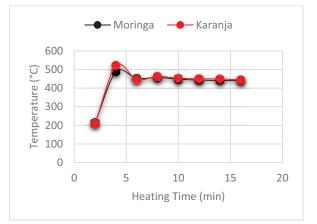


Fig.4 Temperature Changes of Microwave Pyrolysis in 800W

4.3 PYROLYSIS PRODUCT

After microwave pyrolysis, pyrolysis product was obtained. Figure 5 shows bio oil sample of Moringa seed Karanja respectively. Figure 6 shows biochar sample of Moringa seed and Karanja. Liquid product known as bio oil with dark brown colour and good liquidity were converted from microwave pyrolysis process.



Fig.5 Bio oil sample of Moringa and Karanja respectively



Fig.6 Biochar sample of Moringa and Karanja respectively

Refer to Figure 7 and Figure 8, the maximum yield of bio oil for Moringa seed is 12.9 wt% at 13 minutes with

450°C whereas the maximum yield of bio oil for Karanja is 10.6% at 13 minutes with 450°C. The lowest yield of bio oil for Moringa seed is 6.7% at 5 minutes with300°C whereas the lowest yield of bio oil for Karanja seed is 4.8% at 5 minutes with 300°C also. However, another solid product is biochar also known as carbonaceous residue produced in primary and secondary pyrolysis reaction. The maximum yield of biochar for Moringa seed is 66.8% at 5 minutes with 300°C whereas the maximum yield of biochar for Karanja is 69.7% at 5 minutes with 300°C. Pyrolysis gases were visible flow out through the condenser and it was hard to determine the percentage yield. Therefore, the percentage of gas yield was calculated at the difference biomass feedstock and the combination of bio oil and biochar.

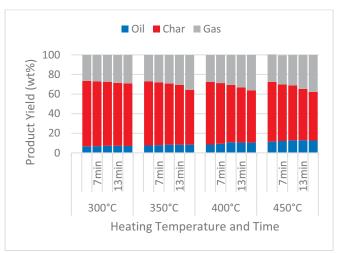


Fig.7 Overall Product Yield of Moringa Seed

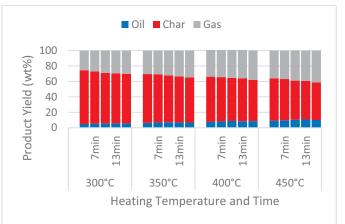


Fig.8 Overall Product Yield of Karanja

4.4 EFFECT OF TEMPERATURE ON PRODUCT YIELD

Various temperature was conducted in this experiment to determine the maximum product yield. Figure 9 show the product yield of Moringa seed in different temperature whereas Figure 10 show the product yield of Karanja in different temperature. However, both graphs showed similar trend. The oil generation increased proportionately to the heating temperature in the microwave pyrolysis up to 450°C. Both raw materials, Moringa seed and Karanja were heated directly by microwave radiation and the samples can reach to high temperature in a short period while the reactor wall was lower temperature than raw materials. The decline in the yield of bio oil when keep rising process temperatures and it suggests that microwave heating is conducive to the secondary cracking reaction (Czarnocka, 2015). However, there is no decrease in percentage yield of bio oil was observed in this experiment when the temperature keeps rising. It means that the pyrolysis temperature in this experiment was not exceed optimal pyrolysis temperature.

When microwave heating at low temperature, the percentage yield of bio oil for both raw materials is the lowest. The reason of low bio oil yield in low temperature is because most of microwave energy was utilized to remove moisture of raw materials and decompose materials before undergo first pyrolysis reaction. It is similar case with the study reported that the bio oil of corn stover was increased with the increased temperature (Zhang et al., 2018).

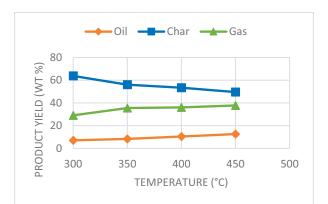


Fig.9 Product Yield of Moringa Seed in Different Temperature

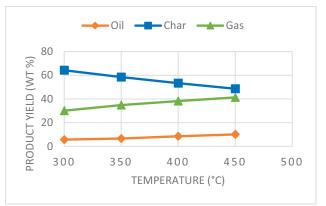


Fig.10 Product Yield of Karanja Seed in Different Temperature

Both graphs show that decreasing of char yield and increasing of gas yield in the same time for both raw materials when temperature increased. The biochar yield decreased more when the temperature reached 350°C for both raw materials. When temperature increased, biochar yield was decreasing sharply due to most lignocellulosic material was decomposed and most volatile fraction had removed during low temperature (Zhao et al., 2017). Therefore, the decrease of char yield is common during pyrolysis due to endothermic reaction of decomposing biomass and heat is provided to the process (Wu et al., 2015). The increasing of gas yield was due to the release of volatile from destruction of organic composition of raw materials during microwave heating.

4.5 EFFECT OF PYROLYSIS TIME ON PRODUCT YIELD

Different pyrolysis time were experimented to determine the product yield in microwave pyrolysis. The experiment keeps repeated to determine the suitable pyrolysis time in order to get the maximum product yield. Figure 11 show the product yield of Moringa seed in different heating time whereas Figure 12 show the product yield of Karanja in different heating time. Based on the graph obtained, both graphs also showed similar trend. Different raw materials treated by microwave pyrolysis at different pyrolysis time produce different bio oil yield. Both graphs showed that both raw materials produce bio oil yield was increased continuously when pyrolysis time was increased. Although increased pyrolysis time resulted initial increased, longer pyrolysis time showed decreases in bio oil yield obtained from both raw materials. Bio oil yield obtained from both raw materials started to decrease slightly after 13 minutes. The bio oil yield of Moringa was 12.6 wt% which decrease of 2.4% whereas the bio oil yield of Karanja was 10.1 wt% which decrease of 4.7%. Long retention time could increase bio oil yield whereas too long retention time could decrease the bio oil yield (Zhang et al., 2017). Another study reported that the oil palm fiber is further increase of the holding time to 33.75 minutes resulted in a pyrolysis liquid oil decrease of 3.3 wt% and therefore, a short time of microwave pyrolysis process shows positive effect to improve the bio oil yield under appropriate condition (Abas et al., 2018; Duan et al., 2018).

Both graphs also showed biochar for both raw materials had an additional decrease after 5 minutes and it showed that primary pyrolysis process start to take over drying process. Solid yield decreased in additional indicated that the degree of pyrolysis was strengthened as pyrolysis time increased (Song et al., 2017). However, samples able to absorb more microwave energy when increased pyrolysis time and pyrolysis can become more complete which results that the decline of residual sample yields.

Gas yield obtained from both raw materials keep increasing when the microwave heating increased. The

maximum gas yield obtained from Moringa seed was 37.8 wt% at 16 minutes with 800W whereas the maximum gas yield obtained from Karanja was 41.3 wt% at 16 minutes with 800W. Both graphs showed that the gas yield of both raw materials further increase after 13 minutes. This is because most of the gas become non-condensable gas and flow out from the condenser when heating time keep increased. High yield of biogas is largely attributed to secondary cracking of volatile. When the residence time of raw materials increase, the condensable vapours decomposed by secondary pyrolysis process to form non-condensable vapours in microwave assisted pyrolysis (Zhang et al., 2017).

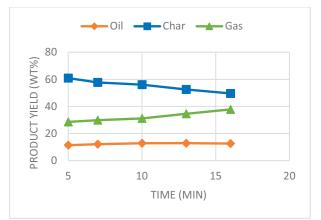


Fig. 11 Product Yield of Moringa Seed in Different Heating Time

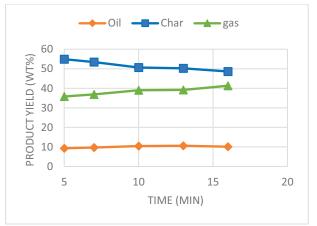


Fig. 12 Product Yield of Karanja in Different Heating Time

4.6 EFFECT OF MICROWAVE POWER ON PRODUCT YIELD

The effect of microwave power level on the product yield during pyrolysis was investigated by using Moringa seed and Karanja. The power was adjusted in different level to determine the maximum product yield for microwave pyrolysis. Figure 13 show the product yield of raw materials in different power level. Based on the graph, it showed that the increased microwave power from 560 W to 800 W which resulted that the yield of bio oil and biogas increased whereas the biochar yield decreased. Karanja has a low biochar yield compare to Moringa seed because Karanja has a higher heating rate than Moringa seed and indicate that high weight loss. The increase in the weight loss was attributed to high heating rates and temperature achieved at higher microwave output power (Wang et al., 2015). Higher pyrolysis rate can improve higher escaping rate of volatile matter from the hot biomass particles and high chance of secondary pyrolysis reactions (Wang et al., 2013).

When microwave power was adjusted to maximum power level that is 800 W, the results show a maximum bio oil vield for both raw materials. Refer to Figure 13. Moringa seed has higher bio oil yield than Karanja. This result show that different raw materials result different bio oil yield although in the same power output level. Although microwave has same power level output, the absorbed energy intensity of samples was different for the different sample masses (Song et al., 2017). Karanja has higher absorbed energy intensity which results higher thermochemical conversion reaction compare to Moringa Seed because Karanja has smaller particles size than Moringa seed. Thermochemical conversion reaction can take place rapidly in smaller size biomass materials (Zhou et al., 2013). Due to rapid thermochemical conversion, Karanja has higher enthalpy energy process and thus it can enhance Karanja undergo secondary thermal cracking period which condensable vapours become non-condensable gas and led to decrease in bio oil yield. A study reported that corn stover with particle size 3mm has higher bio oil with 32.6 wt% whereas particle size 1mm has lower bio oil with 30.5 wt% when heating in same time, power and temperature (Zhu et al., 2018). It is similar case in this experiment which larger particles of raw materials has higher bio oil vield.

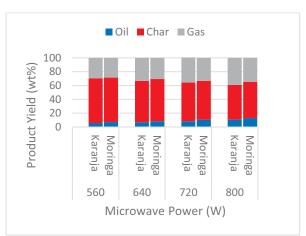


Fig.13 Product Yield for Raw Materials in Different Power Level

Although Moringa Seed has higher bio oil yield, bio gas yield is lower than Karanja. Based on the result obtained, Karanja has higher bio gas yield which is 41.3 wt% but biogas for Moringa Seed is only 37.8 wt%. Both maximum temperature and heating rate increased with decreases particles size of raw materials, no matter the catalyst was added or not (Huang et al., 2018). Moreover, higher heating rate can enhance secondary pyrolysis process occur which means that the vapours released from small particles can further become non-condensable gas. Therefore, biogas yield increase while biochar and bio oil yield decrease for raw materials with small particles.

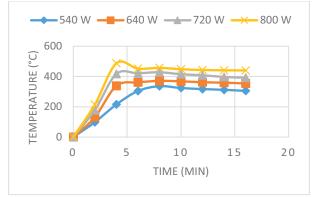


Fig.14 Temperature Profile of Moringa Seed at Different Power Level

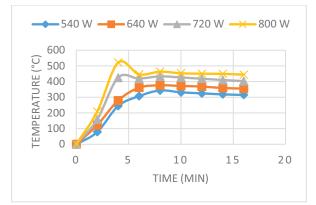


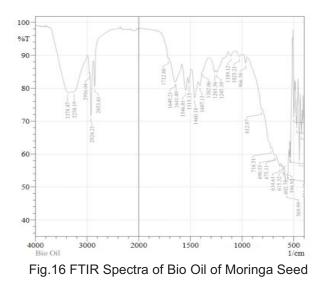
Fig.15 Temperature Profile of Karanja at Different Power Level

Different microwave power can affect different heating temperature and Figure 14 show the temperature profile of Moringa seed during microwave pyrolysis at different power level. Figure 15 show the temperature profile of Karanja during microwave pyrolysis at different power level. Both graphs showed that higher microwave power lead to high heating rate and high temperature. When Moringa Seed was heated with different power level, the heating temperature increased from 336°C at 300 W to 487°C at 800 W. When Karanja was heated with different power level, the heating temperature jurces from 343°C at 300

W to 521°C at 800 W. In microwave power 300 W, bio oil obtained from both raw materials are minimum that is6.7 wt% and 4.8 wt% because low power level produces low temperature during microwave pyrolysis.

4.7 BIO-OIL CHARECTERIZATION

Figure 16 shows the FTIR spectrum of bio oil of Moringa and Figure 17 shows the FTIR spectrum of bio oil of Karanja. O-Hstretching was observed between 3200 and 3600 cm-1 which means that the presence of phenols, alcohols group, proteins, polysaccharides and also presence of oxygenated compounds along with moisture (Bordoloi et al., 2016; Moralı et al., 2016). There are many peaks in between 3200 and 3600 cm-1 which results that the bio oil of Karanja consist high oxvaen content. The C-H stretching between 2850 -3000 cm-1 and C-H bending variations between 1370-1480 cm-1 indicate that the presence of alkanes and methylene groups (CH2) (Liu et al., 2018). The peaks between 1628 - 1815 cm-1 indicated that the C=O group which contained the presence of ketones, aldehydes and carboxylic acid. A study reported that the peak between 1640 and 1750 cm-1 attributed to the stretching vibration of free carbonyl groups of hemicellulose and triglycerides components (Santos et al., 2015).



The peak at 1712.86 cm-1 in bio oil of Moringa Seed and 1637.64 cm-1 for bio oil of Karanja were results the C=O stretching and have been associated with lignin bonds and also attributed to the presence of the aldehydes, ketones and ester groups (Xu et al., 2017), (Lazarri et al., 2018). The peak between 1470 and 1620 cm-1 represent C=C group is indicated the presence of alkenes functional group. The peaks between 1000 and 1370 cm-1 represents phenols and esters which showed the medium vibration C-O stretching for carboxylic acids or esters (Robert et al., 2015). Moreover, absorbance peak in the range of 669 – 915 cm-1 indicate the presence of single, polycyclic and substituted aromatic groups. Lastly, the peak between 500 and 600 cm-1 represents Alkyl Halide compounds which indicated that the presence of C-Br groups.

Table 1 shows the calorific value of bio oil from different raw materials. The calorific value of bio oil for Moringa seed was 25.08 MJ/kg which was obtained under microwave pyrolysis with 800W and 13 minutes heating time. However, the calorific value of bio oil for Karanja was lesser and the result was 20.36 MJ/kg with same parameters.

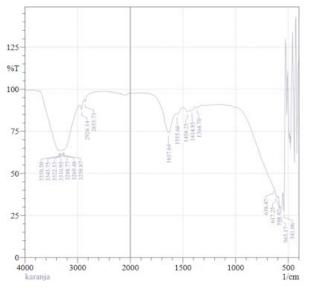


Fig.17 FTIR Spectra of Bio Oil of Karanja

Different biomass in different carbon contents can imply different energy content as the percentage of carbon has major impact on the calorific value (Niebelet al., 2012). A study reported that the comparison for Ponganuaglabra and Mesuaferra seeds, the value for calorific of 16.32 and 18.34 MJ/kg and carbon contents are 44% and 47.5% respectively (Bordoloi et al., 2015). Biomass oil with high carbon content and low hydrogen and oxygen content has higher potential energy. Higher calorific value of bio oil from Moringa was relatively contaminant free with low content of sulphur, oxygen and residue and almost free of metals (Lam and Chase, 2012). Bio oil from Karanja was lower calorific value because it has higher oxygen content in the bio oil. The oxygen content in the fuel can lower the calorific value as oxidizable compounds that are bound in oxygencontaining molecules are difficult to oxidize to a higher oxidation stage. A study reported that calorific value of bio oil of Moringa Seed and Karanja are much lower than commercial fuel such as diesel with calorific value of 45.18 MJ/kg and heavy fuel oil with calorific value of 42.5 MJ/kg which indicated that bio oil content is higher in oxygenated compounds and condensed water (Hawash et al., 2017; Ravikumar et al., 2017). Bio oil of Karanja has lower heating value due to high moisture

content of raw materials during microwave pyrolysis (Ibrahim et al., 2012; Saleh et al., 2023).

Table 1: Calorific Value of Bio Oil from Different Raw			
Materials			

Raw Material	Calorific Value of Bio oil (MJ/kg)
Moringa Seed	25.08
Karanja	20.36

Table 2: pH Value of Bio Oil from Different Raw Materials

Sample	pH Value	
Bio Oil of Moringa Seed	4.38	
Bio Oil of Karanja	5.86	

Table 2 show pH Value of Bio Oil from Different Raw Materials. Bio oil obtained from Moringa seed shows pH value of 4.38 whereas bio oil obtained from Karanja shows pH value of 5.86. A study reported that bio oil obtained from corn stover has a pH value of 2.87 and most of the bio oil have a pH range of 2.0 - 3.8. The main reason for bio oil has low pH value is due to the presence of organic acid such as acetic and formic acid during microwave pyrolysis reaction (Moen et al., 2010).

5. CONCLUSION

This research successfully develop microwave assisted pyrolysis to convert biomass feedstock into bio oil, biochar and biogas. Bio oil was obtained from Moringa seed and Karanja. The optimum bio oil yield was determined by different parameters such as time, temperature and power. The maximum bio yield obtained from Moringa seed was 12.9 wt% at 450°C in the duration of 13 minutes whereas the maximum bio oil yield obtained from Karanja was 10.6 wt% at 450°C in the duration of 13 minutes also. This research showed that bio oil yield increased proportionally with reaction temperature, time and power. When heating time was after 13 minutes, the bio oil of Moringa seed and Karanja were decreased of 2.4% and 4.7% respectively. Functional group of bio oil was detected with FTIR technique and result showed both bio oil contained alcohol, ketone, ester and carboxylic groups. This study shows that the heating value of both bio oil were lower than commercial fuel such as diesel and the pH value of both bio oil were in acidic range.

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REFERENCES

- Abas, F. Z., Ani, F. N., & Zakaria, Z. A. (2018). Microwave-assisted production of optimized pyrolysis liquid oil from oil palm fiber. Journal of Cleaner Production, 182, 404–413. https://doi.org/10.1016/j.jclepro.2018.02.052
- Aboulkas, A., Hammani, H., El Achaby, M., Bilal, E., Barakat, A., & El Harfi, K. (2017). Valorization of algal waste via pyrolysis in a fixed-bed reactor: Production and characterization of bio-oil and biochar. Bioresource Technology, 243, 400–408. https://doi.org/10.1016/j.biortech.2017.06.098
- Al Arni, S. (2018). Comparison of slow and fast pyrolysis for converting biomass into fuel. Renewable Energy, 124, 197–201. https://doi.org/10.1016/j.renene.2017.04.060
- Andreas Niebel., Hugo Balcazar., Thomas Reisch., AngelosLappas., and ChrysaMichailof (n.d.). Feedstock selection, characterization and preparation. Bioboost.Eu. Retrieved March 5, 2023, from

https://www.bioboost.eu/uploads/files/bioboost_d2. 1 avaco2 feedstock selection-vers1.0-final.pdf

- Basak, A., &Uzun, B. (2016). Oeaw.ac.at. Retrieved March 5, 2023, from https://www.oeaw.ac.at/forebiom/WS1lectures/Ses sionII Uzun.pdf
- Bora, M. M., Deka, R., Ahmed, N., &Kakati, D. K. (2014). Karanja (Millettiapinnata (L.) Panigrahi) seed oil as a renewable raw material for the synthesis of alkyd resin. Industrial Crops and Products, 61, 106–114. https://doi.org/10.1016/j.indcrop.2014.06.048
- Bordoloi, N., Narzari, R., Chutia, R. S., Bhaskar, T., &Kataki, R. (2015). Pyrolysis of Mesuaferrea and Pongamia glabra seed cover: characterization of bio-oil and its sub-fractions. Bioresource Technology, 178, 83–89. https://doi.org/10.1016/j.biortech.2014.10.079
- Bordoloi, N., Narzari, R., Sut, D., Saikia, R., Chutia, R. S., &Kataki, R. (2016). Characterization of bio-oil and its sub-fractions from pyrolysis of Scenedesmus dimorphus. Renewable Energy, 98(C), 245–253. https://doi.org/10.1016/i.renene.2016.03.081
- Bridgwater, A. V. (2012). Review of fast pyrolysis of biomass and product upgrading. Biomass & Bioenergy, 38, 68–94. https://doi.org/10.1016/j.biombioe.2011.01.048
- Capodaglio, A. G., Callegari, A., &Dondi, D. (2016). Microwave-induced pyrolysis for production of sustainable biodiesel from waste sludges. Waste and Biomass Valorization, 7(4), 703–709. https://doi.org/10.1007/s12649-016-9496-2

- Cuellar-Nuñez, M. L., Luzardo-Ocampo, I., Campos-Vega, R., Gallegos-Corona, M. A., González de E., &Loarca-Piña, G. Mejía, (2018). Physicochemical and nutraceutical properties of moringa (Moringa oleifera) leaves and their effects in an in vivo AOM/DSS-induced colorectal carcinogenesis model. Food Research International (Ottawa. Ont.). 105. 159 - 168https://doi.org/10.1016/j.foodres.2017.11.004
- Czarnocka, J. (2015). The use of microwave pyrolysis for biomass processing. The Archives of Automotive Engineering, 67(1), 11–21. http://www.aaejournal.com/The-use-of-microwavepyrolysis-for-biomass-processing,99364,0,2.html
- Dewi, H., Saleh, A.A., Reddy, A.N.R., & Hamdan, S. (2018). An Experimental Investigation of Karanja Biodiesel Productionin Sarawak, Malaysia, Journal of Engineering, 2018, 1-8. https://doi.org/10.1155/2018/4174205
- Duan, D., Ruan, R., Lei, H., Liu, Y., Wang, Y., Zhang, Y., Zhao, Y., Dai, L., Wu, Q., & Zhang, S. (2018).
 Microwave-assisted co-pyrolysis of pretreated lignin and soapstock for upgrading liquid oil: Effect of pretreatment parameters on pyrolysis behavior. Bioresource Technology, 258, 98–104. https://doi.org/10.1016/j.biortech.2018.02.119
- Hawash, S. I., Farah, J. Y., & El-Diwani, G. (2017). Pyrolysis of agriculture wastes for bio-oil and char production. Journal of Analytical and Applied Pyrolysis, 124, 369–372. https://doi.org/10.1016/j.jaap.2016.12.021
- Huang, Y.-F., Kuan, W.-H., & Chang, C.-Y. (2018). Effects of particle size, pretreatment, and catalysis on microwave pyrolysis of corn stover. Energy (Oxford, England), 143(C), 696–703. https://doi.org/10.1016/j.energy.2017.11.022
- Ibrahim, N., Jensen, P., Dam-Johansen, K., Ali, R. R., &Kasmani, R. (2012). Influence of reaction temperature and water content on wheat straw pyrolysis. World Academy of Science, Engineering and Technology, International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering.

https://www.semanticscholar.org/paper/dc27c709cf b899c7315c8a790e29b0db44d1478e

- Kan, T., Strezov, V., & Evans, T. J. (2016). Lignocellulosic biomass pyrolysis: A review of product properties and effects of pyrolysis parameters. Renewable and Sustainable Energy Reviews, 57(C), 1126–1140. https://doi.org/10.1016/j.rser.2015.12.185
- Khayoon, M. S., Olutoye, M. A., & Hameed, B. H. (2012). Utilization of crude karanj (Pongamiapinnata) oil as a potential feedstock for the synthesis of fatty acid methyl esters. Bioresource Technology, 111, 175–179. https://doi.org/10.1016/j.biortech.2012.01.177

- Kumar, D., Kumar, A., & Prakash, O. (2012). Pharmacognostic evaluation of stem bark of Pongamiapinnata (L.) Pierre. Asian Pacific Journal of Tropical Biomedicine, 2(2), S543–S546. https://doi.org/10.1016/s2221-1691(12)60270-6
- Lam, S. S., & Chase, H. A. (2012). A review on waste to energy processes using microwave pyrolysis. Energies, 5(10), 4209–4232. https://doi.org/10.3390/en5104209
- Lazzari, E., Schena, T., Marcelo, M. C. A., Primaz, C. T., Silva, A. N., Ferrão, M. F., Bjerk, T., &Caramão, E. B. (2018). Classification of biomass through their pyrolytic bio-oil composition using FTIR and PCA analysis. Industrial Crops and Products, 111, 856– 864. https://doi.org/10.1016/j.indcrop.2017.11.005
- Li, J., Dai, J., Liu, G., Zhang, H., Gao, Z., Fu, J., He, Y., & Huang, Y. (2016). Biochar from microwave pyrolysis of biomass: A review. Biomass & Bioenergy, 94, 228–244. https://doi.org/10.1016/j.biombioe.2016.09.010
- Li, X., Li, K., Li, H., El-Mashad, H., Jenkins, B., & Yin, W. (2017). White poplar microwave pyrolysis: Heating rate and optimization of biochar yield. Bioresources, 13(1). https://doi.org/10.15376/biores.13.1.1107-1121
- Liu, Q., Liu, P., Xu, Z.-X., He, Z.-X., & Wang, Q. (2018). Bio-fuel oil characteristic of rice bran wax pyrolysis. Renewable Energy, 119(C), 193–202. https://doi.org/10.1016/j.renene.2017.12.012
- Liu, R. H., Shen, C. J., Wu, H. J., Deng, C. J., & Liu, S. Y. (2011). Characterisation of bio-oil from fast pyrolysis of rice husk in a fluidised bed reactor. Journal of the Energy Institute, 84(2), 73–79. https://doi.org/10.1179/014426011x129683286253 97
- Lyu, G., Wu, S., & Zhang, H. (2015). Estimation and comparison of bio-oil components from different pyrolysis conditions. Frontiers in Energy Research, 3. https://doi.org/10.3389/fenrg.2015.00028
- Martins, P. F., de Melo, M. M. R., & Silva, C. M. (2016). Techno-economic optimization of the subcritical fluid extraction of oil from Moringa oleifera seeds and subsequent production of a purified sterols fraction. The Journal of Supercritical Fluids, 107, 682–689.

https://doi.org/10.1016/j.supflu.2015.07.031

- Moen, J., Yang, C., Zhang, B., Lei, H., Hennessy, K., Wan, Y., Le, Z., Liu, Y., Chen, P., &Ruan, R. (2010).
 Catalytic microwave assisted pyrolysis of aspen.
 International Journal of Agricultural and Biological Engineering, 2(4), 70–75.
 https://ijabe.org/index.php/ijabe/article/view/165/89
- Moralı, U., Yavuzel, N., &Şensöz, S. (2016). Pyrolysis of hornbeam (Carpinusbetulus L.) sawdust: Characterization of bio-oil and bio-char. Bioresource Technology, 221, 682–685. https://doi.org/10.1016/j.biortech.2016.09.081

- Motasemi, F., Afzal, M. T., Salema, A. A., Mouris, J., & Hutcheon, R. M. (2014). Microwave dielectric characterization of switchgrass for bioenergy and biofuel. Fuel (London, England), 124, 151–157. https://doi.org/10.1016/j.fuel.2014.01.085
- Murray T, D. F. Resende, and G. Luo (2014). Bio-Oil: An Introduction to Fast Pyrolysis and its Applications. Extension Publications. Retrieved March 5, 2023, from https://pubs.extension.wsu.edu/biooil-anintroduction-to-fast-pyrolysis-and-its-applications
- Mushtaq, F., Mat, R., & Ani, F. N. (2014). A review on microwave assisted pyrolysis of coal and biomass for fuel production. Renewable and Sustainable Energy Reviews, 39(C), 555–574. https://doi.org/10.1016/j.rser.2014.07.073
- Nomanbhay, S., Salman, B., Hussain, R., & Ong, M. Y. (2017). Microwave pyrolysis of lignocellulosic biomass—a contribution to power Africa. Energy, Sustainability and Society, 7(1). https://doi.org/10.1186/s13705-017-0126-z
- Ojiako, E. N., & Okeke, C. C. (2013). Determination of antioxidant of Moringa oleifera seed oil and its use in the production of a body cream. Asian Journal of Plant Science & Research, 3(3). https://www.imedpub.com/abstract/determinationof-antioxidant-of-moringa-oleifera-seed-oil-and-itsuse-in-the-production-of-a-body-cream-14256.html
- Ravikumar, C., Senthil Kumar, P., Subhashni, S. K., Tejaswini, P. V., &Varshini, V. (2017). Microwave assisted fast pyrolysis of corn cob, corn stover, saw dust and rice straw: Experimental investigation on bio-oil yield and high heating values. Sustainable Materials and Technologies, 11, 19–27. https://doi.org/10.1016/j.susmat.2016.12.003
- Report with a process scheme for hydrotreating catalytically produced bio-oil and esterifying bio-oil with alcohols and producing fuel gas for power production or synfuels production Deliverable Number: 4.3 Contractual Deadline: M42 Date: 28 March 2013 Author: AV Bridgwater Dissemination status: PU. (n.d.). Geonardo.com. Retrieved March 5, 2023, from https://dibanet.geonardo.com/downloads/d43_diba net%20Process%20for%20BioOil%20treatment%2 0and%20Gas%20production.pdf
- Robert, D.J.K., Silverstein, M., Francis X. (2015), 'Spectrometric identification of organic compounds', Journal of Molecular Structure. 512, Retrieved March 5, 2023, from https://eclass.upatras.gr/modules/document/file.ph p/PHY1973/Silverstein%20 %20Spectrometric%20Identification%20of%20Org anic%20Compounds%207th%20ed.pdf
- Saber, M., Nakhshiniev, B., & Yoshikawa, K. (2016). A review of production and upgrading of algal bio-oil. Renewable and Sustainable Energy Reviews, 58(C), 918–930.

- Saleh, A. A., Hasanuzzaman, M., Cassidy, H., Dayang, S. H., and Shahril, M. (2023). An Exploration of Modified Microwave-assisted Rapid Hydrothermal Liquefaction Process for Conversion of Palm Kernel Shells to Bio-oil. International Journal of Engineering Materials and Manufacture (2023) 8(2) 36-50.
- Salema, A. A., & Ani, F. N. (2011). Microwave induced pyrolysis of oil palm biomass. Bioresource Technology, 102(3), 3388–3395. https://doi.org/10.1016/j.biortech.2010.09.115
- Santos, R. M., Santos, A. O., Sussuchi, E. M., Nascimento, J. S., Lima, Á. S., & Freitas, L. S. (2015). Pyrolysis of mangaba seed: production and characterization of bio-oil. Bioresource Technology, 196, 43–48.
- Song, Z., Yang, Y., Sun, J., Zhao, X., Wang, W., Mao, Y., & Ma, C. (2017). Effect of power level on the microwave pyrolysis of tire powder. Energy (Oxford, England), 127(C), 571–580. https://doi.org/10.1016/j.energy.2017.03.150
- Song, Z., Yang, Y., Zhou, L., Liu, L., & Zhao, X. (2017). Gaseous products evolution during microwave pyrolysis of tire powders. International Journal of Hydrogen Energy, 42(29), 18209–18215. https://doi.org/10.1016/j.ijhydene.2017.04.169
- Wang, N., Tahmasebi, A., Yu, J., Xu, J., Huang, F., &Mamaeva, A. (2015). A Comparative study of microwave-induced pyrolysis of lignocellulosic and algal biomass. Bioresource Technology, 190, 89– 96. https://doi.org/10.1016/j.biortech.2015.04.038
- Wang, N., Yu, J., Tahmasebi, A., Han, Y., Lucas, J., Wall, T., & Jiang, Y. (2014). Experimental study on microwave pyrolysis of an Indonesian low-rank coal. Energy & Fuels: An American Chemical Society Journal, 28(1), 254–263. https://doi.org/10.1021/ef401424p
- Wu, C., Budarin, V. L., Wang, M., Sharifi, V., Gronnow, M. J., Wu, Y., Swithenbank, J., Clark, J. H., & Williams, P. T. (2015). CO2 gasification of bio-char derived from conventional and microwave pyrolysis. Applied Energy, 157(C), 533–539.

- Xu, Z.-X., Liu, P., Xu, G.-S., Liu, Q., He, Z.-X., & Wang, Q. (2017). Bio-fuel oil characteristic from catalytic cracking of hydrogenated palm oil. Energy (Oxford, England), 133(C), 666–675.
- Zhang, Y., Chen, P., Liu, S., Fan, L., Zhou, N., Min, M., Cheng, Y., Peng, P., Anderson, E., Wang, Y., Wan, Y., Liu, Y., Li, B., &Ruan, R. (2017). Microwaveassisted pyrolysis of biomass for bio-oil production. In M. Samer (Ed.), Pyrolysis. InTech.
- Zhang, Y., Chen, P., Liu, S., Fan, L., Zhou, N., Min, M., Cheng, Y., Peng, P., Anderson, E., Wang, Y., Wan, Y., Liu, Y., Li, B., &Ruan, R. (2017). Microwaveassisted pyrolysis of biomass for bio-oil production. In M. Samer (Ed.), Pyrolysis. InTech.
- Zhang, Y., Fan, L., Liu, S., Zhou, N., Ding, K., Peng, P., Anderson, E., Addy, M., Cheng, Y., Liu, Y., Li, B., Snyder, J., Chen, P., &Ruan, R. (2018). Microwaveassisted co-pyrolysis of brown coal and corn stover for oil production. Bioresource Technology, 259, 461–464.

https://doi.org/10.1016/j.biortech.2018.03.078

- Zhao, S., & Zhang, D. (2014). An experimental investigation into the solubility of Moringa oleifera oil in supercritical carbon dioxide. Journal of Food Engineering, 138, 1–10. https://doi.org/10.1016/j.jfoodeng.2014.03.031
- Zhao, S.-X., Ta, N., & Wang, X.-D. (2017). Effect of temperature on the structural and physicochemical properties of biochar with apple tree branches as feedstock material. Energies, 10(9), 1293.
- Zhou, R., Lei, H., & Julson, J. L. (2013). Effects of reaction temperature, time and particle size on switchgrass microwave pyrolysis and reaction kinetics. International Journal of Agricultural and Biological Engineering, 6(1), 53–61.
- Zhu, L., Lei, H., Wang, L., Yadavalli, G., Zhang, X., Wei, Y., Liu, Y., Yan, D., Chen, S., &Ahring, B. (2015). Biochar of corn stover: Microwave-assisted pyrolysis condition induced changes in surface functional groups and characteristics. Journal of Analytical and Applied Pyrolysis, 115, 149–156.