EFFECTS OF MICROWAVE ABSORBERS ON THE PRODUCTS OF MICROWAVE PYROLYSIS OF OILY SLUDGE

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Abstract

The addition of absorber can lead to increase the reaction temperature in the microwave pyrolysis process. Three different sources for microwave absorbers were used to identify the effect of microwave absorber on the product yield from microwave pyrolysis of oily sludge. These absorbers are namely, coconut activated carbon (CAC), palm kernel shell activated carbon (PKSAC) and petroleum coke. The microwave absorbers were added to elevate the temperature of pyrolysis reaction in a nitrogen atmosphere using a modified microwave household reactor. The process included identifying the effect of microwave absorber concentration, and initial moisture content at an optimum sweep gas flow rate on the product yield. The results demonstrated that the addition of CAC, PKSAC and petroleum coke improved the heating rate by shortening the drying process. The results showed that the addition CAC during microwave pyrolysis of oily sludge resulted in the higher gas product distribution compared to other types of absorbers. The results revealed that the addition of 10% of the CAC can pyrolyze oily sludge at a nitrogen gas flow rate of 200 mL/min. At this condition, ~65 wt% of gas was produced for all moisture content of oily sludge samples (4%, 40% and 75%). As well as, this treatment method shortened drying time of oily sludge to 30 minutes. The results showed that higher produced gases of H2 (15%) and CO (13.3%) giving lower heating value (LHV) at 5.57 MJ/m³ were achieved using 10% of CAC in microwave pyrolysis of oily.

Keywords: Microwave, Microwave absorber, Oily sludge, Pyrolysis.
1. Introduction

The oily sludge is an effluent waste product from industries, mainly related in crude oil refining and fuels manufacturing, lubricants and petrochemical intermediates [1]. The quantity of wastewaters and their characteristics highly depends on their origin, the type of oil being processed, process configuration and operation procedure [2]. The treatment of wastewater produced from these activities gives rise to oily sludge. The use of relatively high volumes of water in petroleum refineries, especially for cooling systems encourages the production of surface water runoff and water from cleaning. Eventually, considerable volumes of generating wastewater during processing were reported in ranged from 0.4 to 1.6 times the amount of the crude oil processed [3]. Thus, a total of 33.6 million barrels per day (mbpd) of effluent is generated globally based on the current yield of 84 mbpd [4]. These pollutants can cause significant problems due to its toxicity and hazardous to the environment. As the environmental regulations are increasingly stringent, land farming is becoming less accepted. There are numerous alternatives exist to treat, dispose of or recycle these wastes. The toxic, mutagenic and carcinogenic components in the content of the sludge restricted the release and treatment of oily sludge [5, 6]. Previous studies have been made to convert the oily sludge into useful products such as lower molecule organic compounds and carbonaceous residues by incineration and pyrolysis [7-10].

The most efficient method of oily sludge treatment so far is incineration with energy recovery [11]. A new process of incineration of oil sludge with Coal-Water Slurry (CWS) in an industrial internal Circulating Fluidized Bed (ICFB) boiler was successful in meeting Chinese current environmental requirements [12]. Furthermore, approximately 95% of the ash carried by the flue gas could be recycled as soil farming by the installation cyclone and filter bags. Although incineration can provide a large volume reduction and energy recovery, it leads to toxic emissions into the air, soil and water. On the other hand, pyrolysis process has the ability to produce useful products of choice, namely gas, oil and solid char, which may be used as fuels or a feedstock for petrochemicals and other applications. Various studies on the pyrolysis of biomass have been reported, including agricultural wastes [13], wood sawdust [14], oil palm wastes [15], palm kernel shell [16] and many more.

Microwave heating has been found to be a better alternative to conventional heating methods. It has been widely applied in many fields because of its high heating rate and easy operation [17]. Recently, with the advantages of microwave technology becoming evident as applied in many processes, such technology also has been adapted for the pyrolysis of many kinds of wastes, such as tire powder [18], sewage sludge [19] and organic municipal solid waste [20]. Recently, Chen [21] explored catalytic microwave pyrolysis of crude oil storage tank sludge for fuels using Granular Activated Carbon (GAC) as a catalyst. Generally, pyrolysis is a thermal process of energy conversion in the absence of oxygen to produce a solid (char), liquid (tar) and gas at temperatures above 400-500 °C [22]. In addition, microwave-induced pyrolysis is also possible if the raw material is mixed with an effective receptor of microwave energy such as carbon [23] or certain metal oxides [24]. There have been many studies conducted in the past, combining microwave heating and an absorber, catalyst or additives [25]. However, the effects of microwave absorbers depend on the type and concentration of the absorbers as well.
as the characteristics of the material used. Other parameters such as microwave power, microwave irradiation time, etc., had been studied extensively by others [25]. Therefore, reporting the effect of activated carbon from different sources on the temperature profiles and product yield are significant in this study. The main objective of this study is to investigate the effects of several types of microwave absorbers on temperature and distribution of the gas, liquid and solid products.

2. Materials and Methods

2.1. Oil sludge

Oily sludge was collected from the wastewater treatment of a refinery plant in Melaka, Malaysia. The sludge was treated in a biological sludge storage tank before being dewatered in a drying plant. The dried samples had black colour and semi-solid cake form. These samples were stored in a cold room at a temperature of 4 °C before use in order to retain its freshness and original properties.

2.2. Experimental setup

The experimental setup is shown in Fig. 1. A modified domestic microwave oven (510 mm (H) × 304 mm (W) × 380 mm (D)) was used in this study [26]. A 2.45 GHz magnetron (Samsung M183GN-S, Malaysia) provided with an output power of 850 W. A cylindrical quartz reactor (510 mm height × 40 mm internal diameter) was used for the pyrolysis reaction of oily sludge. It was positioned vertically at the centre of the microwave oven casing. A K-type thermocouple was used to monitor the temperature of the sample during the pyrolysis reaction by connecting it to a data logger system (Pico, TC-08, UK).

Fig. 1. Schematic drawing of the modified microwave oven and the position of the quartz reactor: (1) Magnetron, (2) Quartz reactor, (3) Thermocouple, (4) Oven casing, (5) Quartz distributor plate, (6) Spring for quartz holder fitting, (7) N2 gas inlet, (8) Quartz holder fitting, (9) Cooler system for magnetron, (10) Hole for wave into cavity, (11) Gas outlet, (12) Electrical connection.
2.3. Microwave pyrolysis

The microwave pyrolysis of petroleum sludge was carried out using a modified microwave oven as described in the previous section (2.2). Approximately 15 g of raw oily sludge samples were moulded into a long-cylinder (~6 cm height × ~1.5 cm diameter) form. The absorbers were coated uniformly on the surface area of the moulded sample. The mixture of sample and absorber was placed vertically on the top of distributor plate and quartz holder fitting (labelled as (5) in Fig. 1) before inserting into the quartz reactor through the bottom of the reactor. The cap from the bottom plate was then screwed on properly. A constant flow of carrier gas (N$_2$) was purged into the reactor at a flow rate of 400 mL min$^{-1}$ for 15, and 30 minutes prior and during the experimental runs, respectively. The produced volatile gas from the pyrolysis reaction was passed through two condensers connected to a chiller. The non-condensable gas was collected using Tedlar bag size 12 L at 5 min intervals. The condensed volatile gas was collected as a liquid product; meanwhile, the solid product represents the residue that was left at the end of the reaction.

A 1.5 g (10 wt%) of several microwave absorbers were mixed with the sludge. Coconut Activated Carbon (CAC), Palm Kernel Shell Activated Carbon (PKSAC) and petroleum coke was used as microwave absorbers. The description of these absorbers was illustrated in Fig. 2 and Table 1.

![Fig. 2. Different types of absorbers (a) CAC, (b) PKSAC, and (c) Petroleum coke.](image)

<table>
<thead>
<tr>
<th>Absorber</th>
<th>Shape</th>
<th>Mesh (mm)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAC</td>
<td>Granulated</td>
<td>2.4 × 0.6</td>
<td>KD Technology Sdn. Bhd., Malaysia</td>
</tr>
<tr>
<td>PKSAC</td>
<td>Granulated</td>
<td>2.4 × 0.6</td>
<td>KD Technology Sdn. Bhd., Malaysia</td>
</tr>
<tr>
<td>PC</td>
<td>Granulated</td>
<td>4.6 × 0.7</td>
<td>Waste-water treatment plant, Melaka, Malaysia</td>
</tr>
</tbody>
</table>

2.4. Product recovery

After cooling down the microwave oven to room temperature, the char product was collected from the quartz reactor and all of the absorbers were removed from the char. The solid pyrolyzed sample (with absorber) was first weighed and the produced char was calculated. Since the pyrolyzed oily sludge was readily crumbled, the absorber was manually removed. The char was then kept in a sealed petri dish and stored in a dry cool place for further analysis. The gaseous product
was collected in Tedlar gas bags. Therefore, the weight of the gas product can be calculated by weight difference using the following Eq. (1) [23]:

\[ \text{Gas} \ (g) = \text{Initial mass} \ (g) - \text{Solid char} \ (g) - \text{water} \ (g) - \text{Bio - oil} \ (g) \]

The aqueous fraction was recovered in the 2-neck flasks. Dichloromethane (100%) was used to dissolve the tars adhering to the interior wall of the condensers. The dissolved product was then filtered using filter paper (Whatman, No. 2, UK) and the filtrate was evaporated using a rotary vacuum evaporator (Eyela, N-N series, Japan) at 70 °C for at least one hour. The evaporated filtrate was weighed to obtain the weight of the liquid fraction. Then, it was dried in a drying oven at 105 °C for 24 hours to remove the water content so that the weight of the bio-oil can be obtained. Lastly, 40 mL of dichloromethane was used to dissolve the bio-oil and stored in a refrigerator for further liquid product analysis.

2.5. Characterization of products

The gas product was analysed by injecting 0.5 mL of the gas product in a gas chromatography (Agilent Technologies, HP6890N, US) fitted with TCD and FID detectors. A HP-Molesieve capillary column (30 m length × 0.53 mm internal diameter × 0.50 µm film thickness) was used for the TCD detector. This column was used to detect permanent gases including hydrogen, oxygen, nitrogen, methane and carbon monoxide. The oven temperature was set at 70 °C and the carrier gas (argon) flow rate was set at 6 mL/min. The splitless inlet temperature was 60 °C while the TCD detector was at 200 °C. The TCD chromatogram calibration was carried out using a standard gas mixture (air product, Singapore) containing H₂, O₂, CH₄, CO and CO₂ in nitrogen with a 5 minutes holding time.

A FID detector was used with a GS-Gaspro capillary (J&W Scientific, USA) column (30 m length × 0.32 internal diameter). This column is able to detect hydrocarbon gases from C₁ to C₆. Argon was employed as a carrier gas at a constant flow rate of 3.4 mL/min. The initial oven temperature was 70 °C held for 5 minutes and then programmed to 90 °C at 10 °C/min. Splitless injection was carried out at 120 °C with FID detector at 260 °C. The FID chromatogram calibration was carried out using a standard gas mixture (FLUKA, USA) containing C₁-C₆ straight chain hydrocarbons.

3. Results and Discussion

It was noted in a previous study by Wan et al. [22] that wet sewage sludge is not be heated above 200 °C unless it is mixed with an appropriate microwave receptor. The mixture of the absorber and oily sludge was subjected to the microwave radiation to explore the possible influence of the addition of a microwave receptor.

According to Dominguez et al. [27], there are several important factors that affect the yield and composition of the volatile fraction during pyrolysis liberated such as biomass species [27]. The following subsections discuss the effects of parameters on the pyrolysis operating temperature and product distribution. Due to the obstacle in measuring the real temperature during the pyrolysis, it can be concluded that the real temperature of the inner part of the sample was higher than the observed temperature. This was reported by Chen et al. [28], where the real temperature of the inner part of the sample used was 120 °C higher than that measured by the pyrometer. The measurement was done by inserting a portable
thermocouple into the sample immediately at the end of each run. Finally, the temperature profiles were plotted by taking the average value of obtaining temperature. Mokhtar et al. [29] reported that the main chemical characteristics and its calorific value are summarized in Table 2.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content (%)</td>
<td>75.3</td>
</tr>
<tr>
<td>Proximate analysis (%)</td>
<td>60.6</td>
</tr>
<tr>
<td>volatile matter</td>
<td>8.1</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>28.2</td>
</tr>
<tr>
<td>Ultimate analysis (%)</td>
<td>45</td>
</tr>
<tr>
<td>H</td>
<td>6.6</td>
</tr>
<tr>
<td>S</td>
<td>7.0</td>
</tr>
<tr>
<td>O</td>
<td>1.7</td>
</tr>
<tr>
<td>HHV (MJ/kg)</td>
<td>39.7</td>
</tr>
</tbody>
</table>

*dry basis

3.1. Selection sweep gas flow rate

Oily sludge was pyrolyzed under microwave heating with additional 10% Coconut Activated Carbon (CAC) at different sweep gas flow rates to identify the optimum feeding rate. Nitrogen as the sweep gas was purged through the reactor at three different flow rates of 200, 400 and 600 mL/min to investigate the effect of inert gas on the operating temperature condition and product distribution. Figure 3 shows that there is no apparent effect on the temperature profile when using a flow rate of 400 and 600 mL/min. Both flow rates took approximately 10 minutes for drying purpose at temperature around 100 ºC before temperature increased to around 300 ºC at the 20th minute until the end of the process. Conversely, using a flow rate of 200 mL/min resulted in slightly higher maximum temperature of 321 ºC that was achieved after 20 minutes. Therefore, a nitrogen flow rate of 200 mL/min was used for the rest microwave pyrolysis experiments temperatures.

![Fig. 3. Temperature profile during microwave pyrolysis of oily sludge at different N2 gas flow rate.](image-url)
The highest maximum temperature was achieved at the purged flow rate of 200 mL/min led to a higher gas fraction as presented in Fig. 4. Meanwhile, the reverse trend for tar product could be seen, reflecting that further cracking reactions occurred as follow [30]:

\[
\text{Tar} \rightarrow \text{CH}_4 + \text{H}_2\text{O} + \text{C}_m\text{H}_n + \text{H}_2
\]  

(2)

This is because of higher flow rate that shortens the residence time, thus reducing the chance to be involved with char forming via secondary decomposition of higher-molecular-weight products [31, 32]. Omar et al. [33] seems to opposed the elevation on tar production as the flow rate on their pyrolysis of sugarcane bagasse. However, there is no noticeable trend in solid production.

3.2. Effects of absorber type on the product yield

Tar production could be contributed to the clogging problem in the outlet tubes and coats the wall of reactors, especially during microwave pyrolysis of agricultural biomass [34] and oily sludge as well. The addition of absorber could act to increase the reaction temperature, thus encourage further cracking reactions and minimize the tar production [35]. Several types of absorber were used in this study, namely, Coconut Activated Carbon (CAC), Palm Kernel Shell Activated Carbon (PKSAC) and petroleum coke.

Figure 5 illustrates the temperature profile of oily sludge pyrolysis using different types of absorbers. It was found that performing the microwave pyrolysis of oily sludge without absorber, the achieved maximum temperature was only 250°C. It is worthy to mention that, the drying process took longer time as a result of the relatively slow heating rate. As reported by Kim et al. [36], it is a similar observation. They reported that the maximum attainable temperature was only 200 °C during pyrolysis of sewage sludge under microwave heating without absorber [36]. As expected, the presence of absorbers during the pyrolysis results in to increase the maximum temperature. The addition of petroleum coke seems to shorten the drying time to only 6 minutes compared to 12 minutes for that one that was treated without the absorber. The heating rate was much improved since it took only 8 minutes to reach temperatures of 250 °C before further heating to around 350 °C. A similar trend of the temperature profile for those added with CAC and PKSAC was observed whereby the maximum temperature was 300 °C.
The product yield distribution from the microwave pyrolysis of oily sludge using different types of absorber was shown in Fig. 6. The variety of moisture content in the raw samples might explain the difference since the experiments could not be done within a day. Therefore, the samples might be dehydrated when they were exposed to the environment for a long time resulted in the lower value of the aqueous product from samples that added with petroleum coke. The maximum attainable temperature using petroleum coke samples might be due to two factors. Firstly, the absorbers entirely coated the moulded oily sludge, thus allowing less penetration of the microwave energy [28]. Secondly, because the larger particle size of coke that used in this study delayed the heat transfer from coke to oily sludge [34].

![Fig. 5. Temperature profile during microwave pyrolysis of oily sludge using different types of absorber.](image)

![Fig. 6. Product yield distribution of oily sludge microwave pyrolysis using various types of absorbers.](image)

The gas production for both samples that added with CAC and PKSAC were higher at approximately 65 and 63 wt%, respectively, meanwhile the yield of solid char product was low at about 6 wt% for both CAC and PKSAC. As stated by Yang et al. [37], this is due to the high surface area of the palm kernel shell (927-1100 m$^2$/g) and as suggested by Morf et al. [38], coconut activated carbon (1104.814 m$^2$/g) is able to prolonged the residence time of volatile in hot zone. Consequently, it increased the chance to get involved into the further cracking the volatiles. Compared to the low surface area of petroleum coke which is only 8 m$^2$/g [39]. This might lead to shorter vapor residence time. Due to its higher operating temperature achieved with higher production of gas, CAC was chosen as the
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optimum absorber to perform the rest of the experiments in this study. The experiments aimed to investigate the effects of absorber concentration and initial moisture content on the product yield.

3.3. Effect of absorber concentration

The temperature profile in Fig. 7 shows that the presence of higher CAC in the pyrolysis facilitates the process and achieves the higher temperature at a faster rate. As can be observed, there were no clear plateau in the first 5 minutes for all concentration due to the rapidity of water removal during the drying process. The addition of higher composition of CAC 20% gave faster rise in temperature to 315 °C within 5 minutes and then the temperature remained almost constant at 326 °C until the end of reaction time. It was clearly noted that at the 11th minute, the temperature in the case of 5% addition of CAC, the temperature rose slowly at 1.6 °C/min within the first 10 minutes before reaching the same temperature as the addition of 10% of CAC at 161 °C. However, the temperature raised slower thereafter up to 30 minutes to reach the maximum temperature at about 300 °C. The same trend also has been recorded in previous research on microwave pyrolysis of oil palm empty fruit bunch [26].

Gas is clearly the dominant product for all cases, but it was a bit higher in both cases of 5 and 10% addition of CAC, as shown in Fig. 8. Increasing the microwave absorber did not improve the gas production, but volume reduction of solid product and a very low tar formation were noted. This might be attributed to two factors. Firstly, the initial water content of the sludge was higher, so the solid fraction was lower compared to the cases of 5% addition of CAC. This occurred due to the escaping of water molecules from the sludge during the storage. Secondly, the high heating rate might favor the secondary cracking reactions as explained in Eqs. (2) to (4) [39]. Thus, the addition of 10% CAC during microwave pyrolysis of oily sludge was chosen as the best absorber composition in order to obtain higher gas product distribution. The gas production equations can be seen in the following:

\[ \text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \quad (3) \]
\[ \text{C} + \text{CO}_2 \rightarrow 2\text{CO} \quad (4) \]
\[ \text{C} + \text{H}_2 \rightarrow \text{CH}_4 \quad (5) \]

Fig. 7. Temperature profile during microwave pyrolysis of dried oily sludge using different concentration of CAC as absorber.
3.4. Effect of initial moisture content

Three different levels of the initial moisture content of oily sludge were used in the microwave pyrolysis with the addition of 10% of Coconut Activated Carbon (CAC). These levels were 4% moisture, 40% moisture and 75%. The oily sludge was dried for 24 and 6 hr in a drying oven at temperature 105 °C to get 4 and 40% moisture content, respectively, while untreated oily sludge with 75% moisture content was used for a comparison. The temperature profile is shown in Fig. 9. For the case of 4% moisture, the temperature was raised slowly at 8.2 °C/min until it reached the maximum temperature of 263 °C after 30 minutes. The oily sludge with 40% moisture had similar trend only up to 100 °C before starting to rise rapidly until it reached a temperature at around 300 °C within 26 minutes, which is slightly lower than that of untreated sludge. This probably due to the lesser energy needed to evaporate a lesser amount of water molecule. This possibly according to the difficulty of the oily sludge to absorb microwave energy since only a small amount of water molecule presents in the sludge. However, in overall there is no obvious difference in the maximum attainable temperature reaction although different heating rate trend could be seen.

These differences in temperature trend resulted in the different products fraction in dry basis as shown in Fig. 10. Nonetheless, the gas production for all cases of 4%, 40% and 75% moisture was about at the same value at ~65 wt%. Therefore, there was the very low volume of tar was produced from these cases. Meanwhile, the 4% moisture sample only yielded 60 wt% gas, probably because of the low temperature, which did not allow the secondary cracking reactions to occur and lead to higher tar yield (6.8%). As expected, the highest volume reduction was observed in samples with the highest moisture content (75% moisture) whereby only a small amount of solid product left after the pyrolysis. The amount of aqueous produced is directly proportional to the moisture content of each sample.
A mass balance calculation for the product gas was performed and the results are tabulated in Table 3. A 10% of the CAC addition produced the highest H\textsubscript{2} (15%) and CO (13.3%) concentrations, giving high value of the Lower Heating Value (LHV) as calculated using Eq. (6) [27].

\[
LHV_{gas} = (30x_{CO} + 25.7x_{H2} + 85.4x_{CH4} + 151.3x_{CnHm}) \times 4.2
\]  

(6)

However, the gas started to produce later compared to other concentrations (Fig. 11). Increasing the concentration of CAC to 20% did not increase the gas concentration except for CH\textsubscript{4} (1.67%). The reason it might be because a thick coating of CAC on the surface of the sample might avoid the direct penetration of the microwave energy into the sample. As reported by Chen et al. [28], consequently, this would suppress gas production. The addition of 10% CAC during the pyrolysis had promoted the reaction as in Eq. (4). The LHV of 10% CAC addition was 5.57 MJ/m\textsuperscript{3} as compared to 0.18 and 1.57 MJ/m\textsuperscript{3} from 5 and 20% addition, respectively. As reported by Karayildirim et al. [40], this value was lower than what they reported, where gas product gave a high gross calorific value of
about 35.8 MJ/m$^3$. Meanwhile, the heating values of gas produced from microwave pyrolysis of sewage sludge were 12.8 to 13.6 MJ/m$^3$ whereas from conventional pyrolysis the value ranged from 15.2 to 17.4 MJ/m$^3$ [41]. However, Menendez et al. [42] reported that the heating values of the gases from microwave pyrolysis of sewage sludge ranged from 6.6 to 8.6 MJ/m$^3$.

Table 3. The product gas distribution at different absorber concentration.

<table>
<thead>
<tr>
<th>Absorber concentration</th>
<th>Gas produced (mol%, dry, N$_2$-free basis)</th>
<th>Gas Yield (m$^3$/kg oily sludge)</th>
<th>LHV (MJ/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H$_2$</td>
<td>CH$_4$</td>
<td>CO</td>
</tr>
<tr>
<td>CAC 5%</td>
<td>0.10</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>CAC 10%</td>
<td>15.00</td>
<td>1.06</td>
<td>13.29</td>
</tr>
<tr>
<td>CAC 20%</td>
<td>3.27</td>
<td>1.67</td>
<td>1.43</td>
</tr>
</tbody>
</table>

Figure 11 shows the evolution of the permanent gas from microwave pyrolysis of oily sludge using CAC as an absorber for 5 minutes interval. It was noted that for 10% CAC addition, the gas started to produce within 15 minutes of reaction, then peaked at within 25 minutes for H$_2$ (8.63%) and 20 minutes for CH$_4$ (2.2%) and CO (2.85%) gases. At all CAC concentrations, the gas production reduced after the 30th minutes when there were no more gases produced. However, as the production of CO using 5% CAC fluctuated during the pyrolysis, it was observed that CO gas still produced at the 35th minutes. 20% CAC addition resulted in lower production of all gases although the reactions were faster at the 10th minutes compared to 15th minutes for 10% CAC addition.

Figure 12 shows the evolution of hydrocarbon gases from microwave pyrolysis of oily sludge with a 10% CAC addition. All the hydrocarbon gases peaked at the 10th minute except CH$_4$, which peaked at 25 minutes. It could be seen that CH$_4$ production kept increasing until the 25th minute, then reduced after the 25th minutes. The concentrations of ethane, ethylene, propane and propylene remained almost constant at 10 to 25 minutes but the increment of propylene concentration after the 30th minute also could be noticed. Iso-butane and n-butane could be traced during the pyrolysis after within the 10th minutes to 25th minutes. The dehydrogenation of ethane into ethylene and propane into propylene might contribute to the higher concentration of H$_2$ [26].

3.5. Characteristics of bio-char

The chemical characteristics of the char produced in this study are tabulated in Table 4. These results were compared to those obtained by previous researches [22, 40, 43]. The suitability and safety of the char to be disposed-off by landfill method, or either incinerated or used as absorbents depends on their physical and chemical characteristics. The char obtained from the microwave pyrolysis showed a high ash content (51.14%), which makes them not suitable to be used as fuel. The moisture content was found to be about 2 times higher (4.22%) compared sewage sludge chars (1.8 to 2.9%) but a bit lower than that of EFB chars (6.8%). This possibly due to the high moisture content in the raw sample and incomplete drying and heating processes during the pyrolysis. However, this could be a good candidate for microwave absorber. The high carbon (60.52%) coupled with high oxygen (21.49) compared to
the oil palm empty fruit bunch (EFB) and sewage sludge were expected to give a positive impact on the HHV, but the high content of oxygen (21.49%) might be the reason to the lower HHV and possibly highly oxygenated liquid and solid products. Although the char calorific value was higher (7.03 MJ/kg) than that of the sewage sludge char (5.85 MJ/kg), actually the value was as lower as 3 times compared to the energy in other biomass such as empty fruit bunch char [26].

Fig. 11. Product gas profile of microwave pyrolysis of oily sludge using CAC as absorber.
Fig. 12. Evolution of hydrocarbon gases from microwave pyrolysis of oily sludge with 10% CAC addition.

Table 4. The proximate and ultimate analyses of pyrolytic char.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Oily sludge (in this study)</th>
<th>Agricultural waste (EFB)</th>
<th>Sewage sludge$^{b,c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content</td>
<td>4.2</td>
<td>6.8</td>
<td>6.8</td>
</tr>
<tr>
<td>Proximate analysis (wt%, db)</td>
<td>44.7</td>
<td>15.2</td>
<td>2.8 - 53.9</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>0.00</td>
<td>68.8</td>
<td>nd</td>
</tr>
<tr>
<td>Fixed carbon ash</td>
<td>51.1</td>
<td>16.0</td>
<td>36.9 - 84.5</td>
</tr>
<tr>
<td>Ultimate analysis (wt%, db)</td>
<td>Solid density (g cm$^{-3}$)</td>
<td>56.7</td>
<td>15.4 - 36.6</td>
</tr>
<tr>
<td>C</td>
<td>3.4</td>
<td>1.98</td>
<td>0.0 - 4.8</td>
</tr>
<tr>
<td>H</td>
<td>1.1</td>
<td>1.09</td>
<td>0.4 - 4.0</td>
</tr>
<tr>
<td>N</td>
<td>13.5</td>
<td>na</td>
<td>0.4 - 0.9</td>
</tr>
<tr>
<td>S</td>
<td>21.5</td>
<td>40.2</td>
<td>0.0 - 18.7</td>
</tr>
<tr>
<td>O (by difference)</td>
<td>Solid density (g cm$^{-3}$)</td>
<td>7.0</td>
<td>21.5</td>
</tr>
<tr>
<td>CV (MJ/kg)</td>
<td>1.5 - 1.6</td>
<td>na</td>
<td>5.9</td>
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</tbody>
</table>

$^{db}$ – dry basis; $^{na}$ – not available; nd – not defined; EFB – empty fruit bunch
Sources: $^{a}$[27]; $^{b}$[43]; $^{c}$[20].

4. Conclusion

The addition of Coconut Activated Carbon (CAC), Palm Kernel Shell Activated Carbon (PKSAC) and petroleum coke improved the heating rate by shortening the drying process. Although the maximum attainable temperature from the added sample with petroleum coke was the highest, lowest gas product was collected (59%). Gas production for both samples added with CAC and PKSAC were of the same value of approximately 64%. The addition of the highest concentration of CAC at 20% gave the fastest temperature rise to 315 ºC at 61.5 ºC/min within 5 minutes with a maximum temperature of 326 ºC. However, the gas concentration remained low except for CH4 (1.67%). In fact, 10% CAC addition produced the
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highest H₂ (15%) and CO (13.3%) concentrations giving a high value of the Lower Heating Value (LHV) at 5.57 MJ/m³ as compared to 0.18 and 1.57 MJ/m³ from 5 and 20% addition, respectively. These results suggest that the modified lab-scale microwave oven was successfully used to dry and pyrolyze oily sludge simultaneously. For further studies, the study suggests performing the cost analysis based on microwave absorber type and product yield.

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