Doping of Potassium Hydroxide and Calcium Oxide on Synthesized High Surface Area Activated Carbon for Transesterification of Waste Cooking Oil

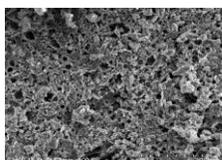Kevin Chee Kai Wen*, Muhammad Azam Muhammad Zaki and Abdul Rahim Yacob

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GRAPHICAL ABSTRACT

Micrograph of KOH-CaO-Catalyst with magnification 500X

ABSTRACT

Transesterification is a process where triglyceride is converted to fatty acid methyl esters or biodiesel. High surface area activated carbon was successfully prepared from palm kernel shells (PKS) to act as the catalyst support via chemical activation with potassium hydroxide (KOH) as an activating agent and later doped with calcium oxide (CaO). Thermal gravimetry analysis (TGA) proved that the optimum activation temperature of PKS is 600 ºC. The optimization of the concentration of potassium hydroxide was done according to four different concentrations at 15%, 20%, 25% and 30%. Under FTIR analysis, the missing of O-H bond and sp^3 carbon bond stretching in the activated char suggested that the activated carbon was successfully produced. At potassium hydroxide concentration of 25%, it was found that the BET surface area was the highest, in which it achieved 443.83 m^2/g. Field emission scanning electron microscopy (FESEM) analysis also proved the formation of porous structure with high surface area. The prepared activated carbon is doped with potassium hydroxide and calcium oxide (KOH-CaO-Catalyst). The FTIR analysis show the missing of sp^2 carbon bond stretching, C=C bond and C-H bond bending, which deviated from the activated carbon. FESEM analysis also proved that the surface of the activated carbon was impregnated with KOH and CaO. The catalyst was then used for the transesterification reaction of waste cooking oil with excess methanol. The ratio of methanol to waste cooking oil used was 20:1. The fatty acid methyl ester (FAME) yield from transesterification was 99.5%. In this study, the optimum parameters to prepare high surface area activated carbon for transesterification of waste cooking oil was at 600ºC activation temperature with 25% of KOH concentration.

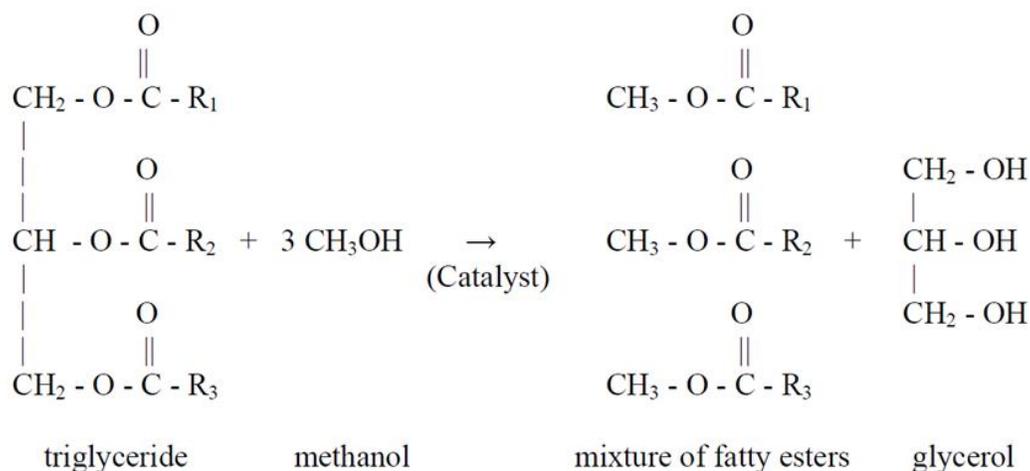*Keywords: activated carbon, palm kernel shells, catalyst, transesterification*

1.   INTRODUCTION

Palm kernel shell (PKS) is discovered to be a good material to produce activated carbon, either by physical or chemical activation. The physical activation is defined as a dual-step process that starts with carbonization (pyrolysis) in the presence of inert gas and later the resulting char is activated [1]. Activated carbon is defined as an amorphous carbonaceous material which exhibits a very disordered microcrystalline structure where it shows no regular or fixed atomic structure like an elemental carbon [2]. There are a lot of activation agents involving the preparation of activated carbon, such as zinc chloride, phosphoric acid, sodium hydroxide, iron chloride [3]. When compared to these activation agents, potassium hydroxide (KOH) is eco-friendlier. PKS-based activated carbon is said to be a good absorbent as research done shows that PKS has the capability in an effective approach of defluorination [4].

2.   EXPERIMENTAL

The experiment was divided into three main stages. The first stage focused on preparation of activated carbon from palm kernel shells. First of all, the pre-treatment of raw PKS was done. The PKS was washed with water for 3-4 times to remove soil and dirt, followed by washing with diluted hydrochloric acid (HCl) to dissolve unwanted particles. After that, the PKS was washed with water for 3-4 times again to remove the HCl. Then the PKS was dried in an oven at temperature around 110ºC overnight. For the activation with KOH, 20g of PKS was mixed with 3g of KOH (15% by weight of PKS). The mixture of PKS and KOH solution was homogenised using a hot plate for 5 hours. The homogenised mixture was dried in the oven at temperature around 110ºC overnight. In calcination step, the dried mixture was weighted and transferred to a crucible and calcined in a furnace at various temperatures

(500°C, 600°C, 700°C) for 2 hours. After that, the biochar was collected. The biochar was filtered over a filter paper with hot distilled water until the pH of the filtrate was 7 (to remove KOH). The biochar was then dried in the oven at temperature at 110°C for at least 24 hours. After that, the activated carbon collected was weighted and grounded. The second step involved the impregnation of KOH and CaO. The prepared AC with the highest surface area is impregnated with KOH and CaO. KOH and CaO were both weighed 25% of total weight of AC used, and were added to the AC. The mixture was stirred for 5 hours using a magnetic stirrer and dried overnight in the oven. The third stage was the transesterification reaction. Transesterification was carried out in a 250 mL two-necked round bottom flask equipped with a reflux condenser and magnetic stirrer. The flask was immersed in paraffin oil to control the reaction temperature. The ratio of the methanol to waste cooking oil is set to be 20:1.


Scheme 1 Transesterification reaction between triglyceride and methanol.

3.   RESULTS AND DISCUSSION

3.1   Characterization of Activated Carbon

From Figure 1, there are a few stages of decomposition of raw palm kernel shells. Stage I is due to the weight loss of moisture ranging from 100 to 150 °C. However, the weight loss is not significant, which consist of only 0.34%. This is different from a research reported that PKS contains 9.4% of moisture [7]. This may due to the different pre-treatment done to the PKS. In this research, the grinded pre-treated PKS was dried in an oven at 110 °C before any characterization was conducted. For temperature ranged from 150 to 400 °C, there is a weight loss most probably due to the loss of volatile matters. In the range between 150 °C and 320 °C and the range between 320 °C and 400 °C, they are suggested to be the decomposition of hemicelluloses and celluloses, respectively, whereas the degradation of lignin above 280°C [8]. The total of this volatile matters contributes to 53.81%. From the thermogravimetry analysis, the fixed carbon obtained contributes to 34.12% at 600 °C. Weight loss from 400 to 600 °C is 13.54%, while from 600 to 1000 °C, 13.73% weight is lost. The high ash percentage of 13.54% in this study may due to the high content of inorganic and non-combustible materials [9].
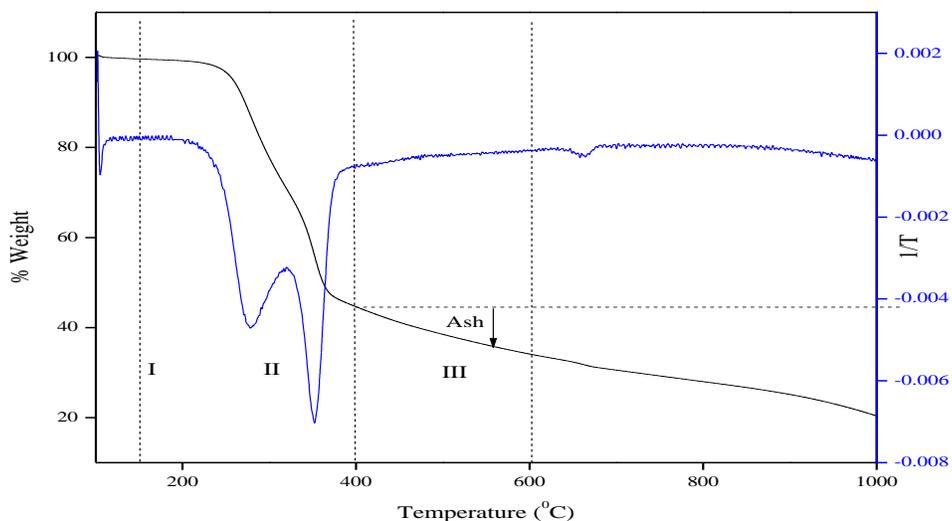
Figure 1 TGA/DTG curves of raw PKS.

TGA in Figure 1 also shows that above 400 ºC, most of the organic compound in the palm kernel shells was decomposed. This indicates that the carbon can be carbonized with a minimum temperature of 400 ºC. The activation energy was selected to be 600 ºC due to it was more suitable for the preparation of higher surface area activated carbon which was activated by alkali metal. This is because, the higher the temperature, the higher the rate of gasification occurred on the surface of the carbon.
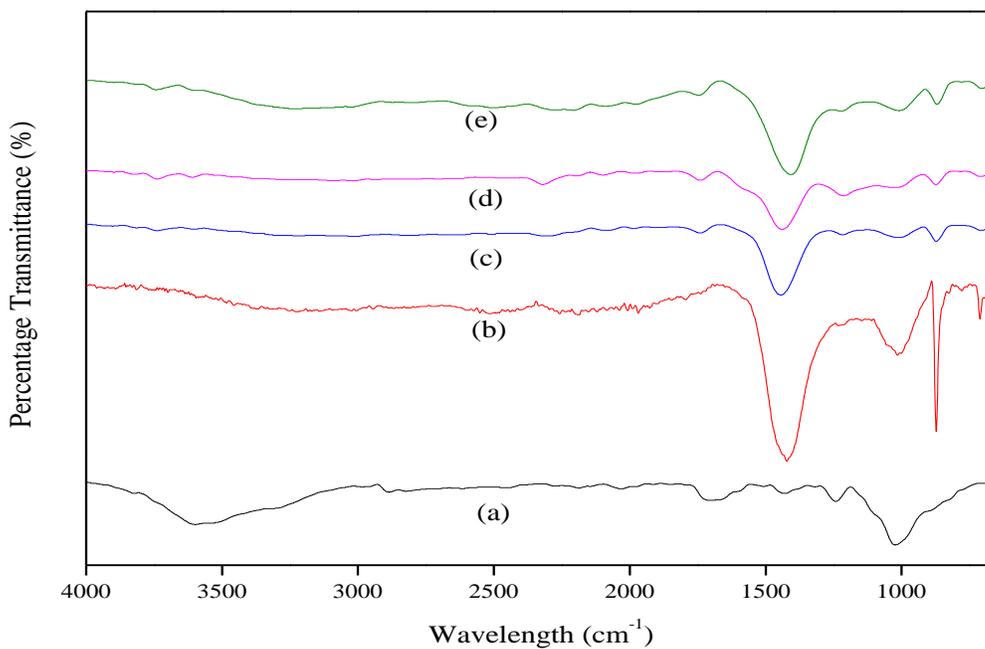
Figure 2 FTIR spectra for (a) Raw-PKS, (b) AC-15%, (c) AC-20%, (d) AC-25%, and (e) AC-30%.

Table 1 ATR-FTIR spectra band and the type of functional group

Peak Assignment	Wavenumber (cm^{-1})				
	Raw PKS	**AC-15%**	**AC-20%**	**AC-25%**	**AC-30%**
O-H bond stretching	3612	-	-	-	-
C-H bond stretching (sp3)	2883.8	-	-	-	-
C-H bond stretching (sp2)	-	3020	3012.5	3027.8	3000
C=O bond stretching	1721.2	-	1740	1746	1743.3
C=C bond stretching	-	-	1650	1680	1675
C-H bond bending	1424.6	1422.4	1445.1	1437.6	1406.9
C-O bond stretching	1253.8, 1020.0	1230.4, 1013.5	1218, 1010.8	1215.5, 1021.4	1216.8, 1008.2
C=C bond bending	-	870.8	873.4	874.2	870
C-H bond bending	-	707.9	713.7	717.1	703.4

For chemically prepared activated carbon, they differ a lot from the raw PKS. First of all, it can be observed in Figure 2 and Table 1 that there are some peaks which are missing in AC-15% to AC-30% when compared to the raw PKS. Such absorption peaks are the O-H bond stretching and the sp^3 C-H bond stretching. The missing O-H stretching might due to the removal of water molecules from the PKS. Since the reaction involves high temperature calcination, and the prepared carbons are kept dry all the time, hence it is reasonable for the O-H stretching to be absence. Besides, there are some addition of absorption peaks to the chemically prepared activated carbon: C=C bond bending and C-H bond bending at the fingerprinting region. From the spectra obtained, C=C bond bending is ranged between 870 and 875 cm^{-1}, while C-H bond bending is ranged from 703.4 to 717.1 cm^{-1}. The presence of weak absorption peaks in the range between 1650 and 1680 cm^{-1} also prove the existence of aromatic C-C double bonds which is supported by the presence of sp^2 C-H bond stretching in the range between 3000 to 3030 cm^{-1}. This absorption can sturdily suggest the presence of activated carbon since volatile organic compounds are removed and the reduction of the functional groups. However, for AC-15%, it shows a small difference from the other activated carbon. It shows none of the C=O and C=C aromatic stretching. This might due to the insufficient concentration of potassium hydroxide to activate the raw PKS. AC-20%, AC-25% and AC-30% all show a similar pattern in their spectra. Hence it can be deduced that AC-15% with only 15% of potassium hydroxide concentration is not suitable for the preparation of activated carbon.

Table 2 BET surface area of PKS and activated carbon at different temperatures

Activation temperature (°C)	BET surface area (m^2/g)
Raw PKS	1.79
500	219.32
600	269.09
700	N/A

Table 3 BET Surface Area with respect to different concentration of KOH

| Concentration of potassium hydroxide (weight percentage % of PKS)	BET surface area (m^2/g)
0	1.79
15	269.09
20	279.42
25	443.84
30	3.17

Table 2 shows that raw PKS has only a small surface area of 1.79 m^2/g, this is due to the present of cellulose, hemicellulose and lignin present on the surface of the palm kernel shells. From Table 2, it can be observed that with increasing of temperature, the surface area of the activated carbon increases. However, the activation calcination at 700°C had totally disrupted the PKS structure and only ash was found after the calcination. Calcination at 600°C has the highest surface area obtained, which is 269.09 m^2/g.

Another parameter was set, which is the concentration of the activating agent used. In this research, potassium hydroxide was used as the activating agent. For the result in Table 2, the concentration of potassium hydroxide was kept constant at 15% weight of the PKS used. As for result in Table 3, the variation of the KOH's concentration is from 15% to 30% at constant temperature 600°C. From the table, it can be observed that the surface area of the activated carbon increases when the concentration of potassium hydroxide increases. The surface area increased to 443.84 m^2/g at 25%. The increase in the activated carbon is mainly due to the gasification in which partially or all volatile matters are eliminated, resulting the formation of pores on the activated carbon structure.

(a)

(b)
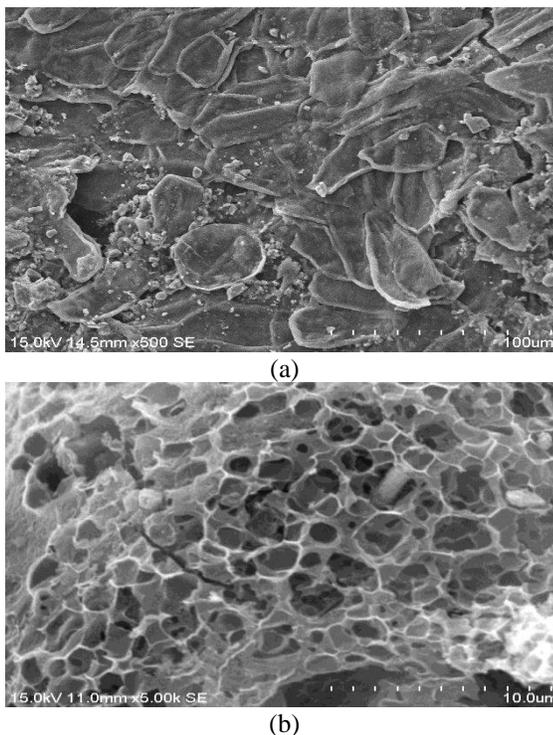
Figure 3 Micrographs of (a) Raw PKS with magnification of 500X, (b) AC-25% with magnification of 5000X.

3.2   Characterization of KOH-CaO Impregnated Catalyst

From Figure 4 and Table 4, the spectrum of KOH-CaO-Cat exhibits almost similar pattern with the spectrum of AC-25%. This is because the catalyst is produced from AC-25%. However, there are some peaks that are absent in the catalyst. One of it is the stretching of sp^2 C-H bond around 3000 cm^{-1}, which exhibited by AC-25% at 3027.8 cm^{-1}. Besides, the catalyst also has no aromatic C double bonds absorption peak. The lack of these two peaks might indicate the absent of aromatic C=C bonding. Doping of KOH and CaO into the activated carbon has chemically change the surface structure of the activated carbon.
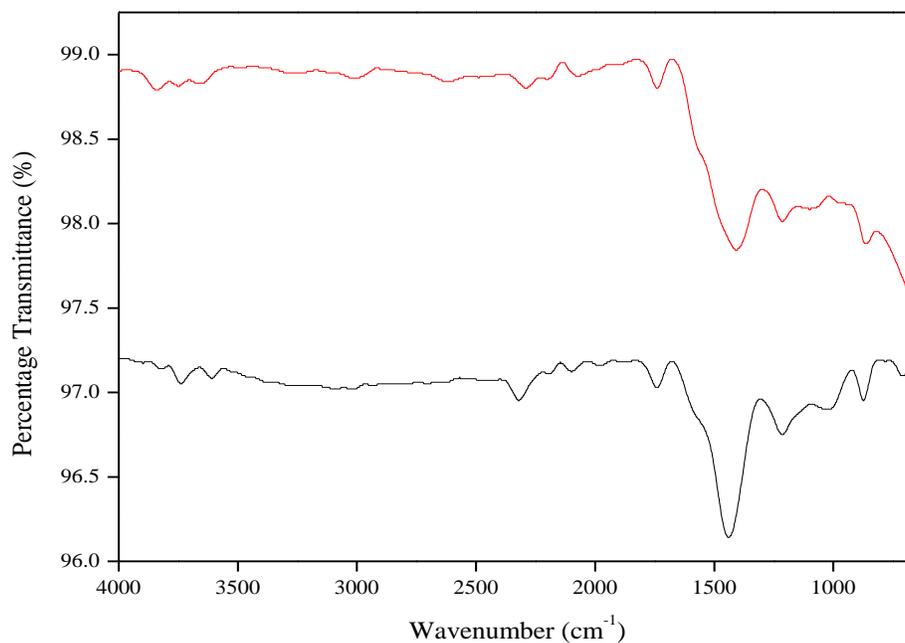
Figure 4 FTIR spectra for (a) AC-25%, (b) KOH-CaO-catalyst.

Table 4 FTIR spectrum band and the type of functional groups

Peak Assignment	Wavenumber (cm^{-1})	
	AC-25%	**KOH-CaO-Cat**
C-H bond stretching (sp^2)	3027.8	-
C=O bond stretching	1746	1740.3
C=C bond stretching	1680	-
C-H bond bending	1437.6	1409.2
C-O bond stretching	1215.5, 1021.4	1221.3
C=C bond bending	874.2	878.2
C-H bond bending	717.1	-

FESEM analysis was applied to study the surface morphology, size and shapes of the raw PKS, AC-25% and KOH-CaO-Catalyst. Figure 3 and 5 shows the FESEM micrographs of PKS and AC-25%, and KOH-CaO-Catalyst, respectively.
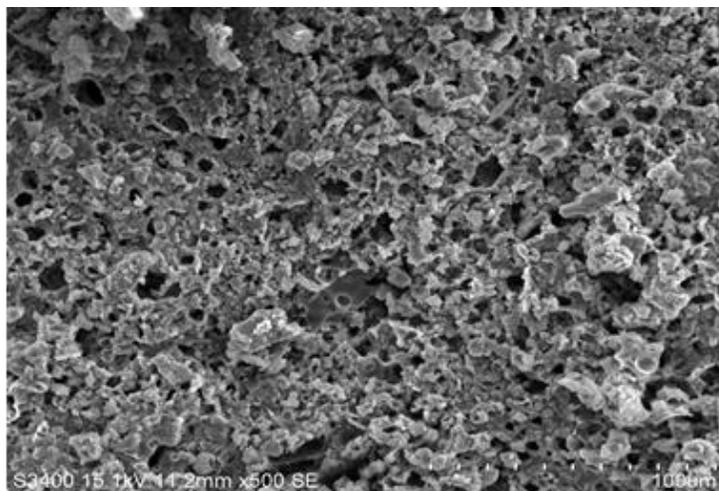

Figure 5 Micrograph of KOH-CaO-catalyst with magnification 500X.

The activated carbon's pores can be seen blocked by foreign particle, which in this study, the potassium hydroxide and calcium oxide. The blockage of the pores indicates the success of the impregnation of potassium hydroxide and oxide onto the surface or into the pores of the activated carbon. Hence, in other words, the activated carbon with high surface area is suitable to be used as a support for potassium hydroxide and calcium oxide catalyst.

3.3   Basicity of Activated Carbon and KOH-CaO-Catalyst

The basicity of AC-25% is 0.72 mmol/g, which is lower than that of KOH-CaO-Cat, which exhibits 1.34 mmol/g of basicity. The result is logical since the KOH-CaO-Cat contains twice amount of base in it than that of AC-25%.

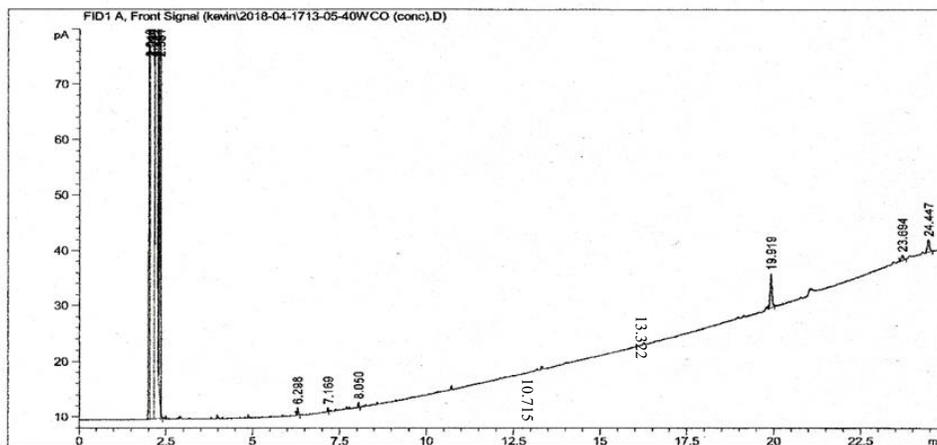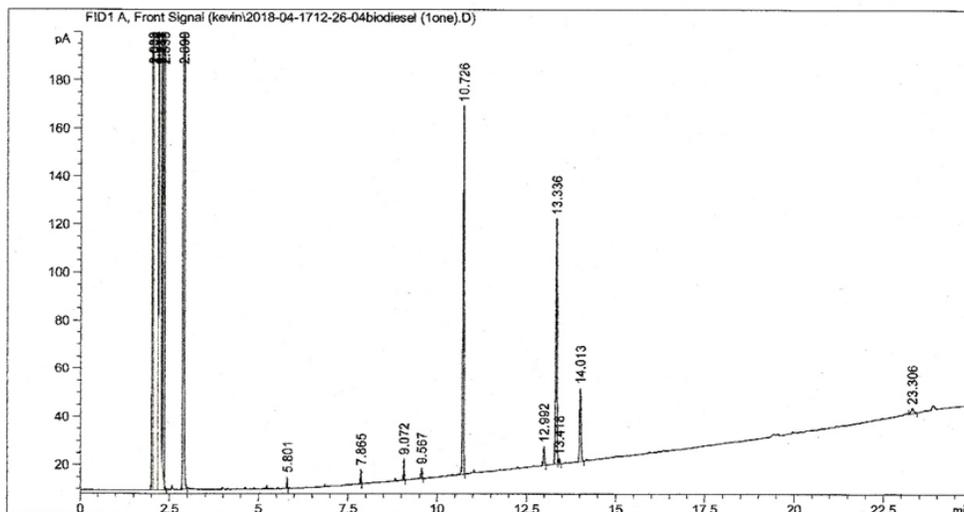3.4   Transesterification Reaction of Waste Cooking Oil

Figure 6 GC-FID chromatogram for waste cooking oil

Figure 7 GC-FID Chromatogram for biodiesel.

Table 5 shows the corresponding retention times of both waste cooking oil and biodiesel while Figure 6 and Figure 7 illustrate the GC-FID spectra of waster cooking oil and biodiesel respectively. The peak at which myristic acid exhibits is chosen for FAME yield calculation because it has the highest and apparent peak. The percentage of FAME yield for the transesterification of waste cooking oil is 99.5%. This shows that the transesterification reaction did take place since the conversion of biodiesel was 99.5% after a 4 hour and reaction at 65 ℃.

Table 5 Correspond retention times of waste cooking oil and biodiesel

Peak Assignment	Retention Times, min	
	Waste Cooking Oil	Biodiesel
Lauric Acid	8.050	7.865
Myristic Acid	10.715	10.726
Ginkgolic acid	13.322	13.336
Erucic Acid	23.694	23.306

4.   CONCLUSION

In this study, all the objectives were successfully achieved. Firstly, the preparation of high surface area activated carbon from palm kernel shell was successfully performed using potassium hydroxide as an activation agent. The BET surface area of the activated carbon prepared was 443.84 m^2/g. The activated carbon was also verified by the TGA and FTIR analysis. The FESEM result further proved that porous and amorphous structures were formed. The optimum carbonization temperature for PKS to be converted into activated carbon was 600 ℃ with 25% (weight percentage of PKS) of potassium hydroxide. Secondly, the impregnation of potassium hydroxide and calcium oxide onto the surface of the prepared activated carbon was also successfully achieved. The FTIR analysis showed that some missing peaks indicated that the doping of KOH and CaO was successful due to the changing in structure to the activated carbon. FESEM micrograph also proved the present of KOH and CaO onto the surface of the amorphous activated carbon. An increase in the basicity of the KOH-CaO-Catalyst from its previous state which was activated carbon also shows that the impregnation was accomplished. Lastly, the prepared catalyst was successfully applied in transesterification of waste cooking oil. GC-FID was used to analyse the biodiesel produced. The FAME yield of the transesterification reaction was 99.5%. This shows the catalyst is suitable for the transesterification reaction.

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