Journal of Engineering and Applied Sciences 11 (11): 2508-2513, 2016
ISSN: 1816-949X

Transesterification of Waste Frying Oil (WFO) using Waste Chicken Bone as a Catalyst

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Abstract: Abundant of waste animal bones can be found especially in restaurant and wet market. In fact, waste animal bones contributed to huge number of our daily municipal waste. Most of these wastes are being thrown away without any proper treatment of disposal. Animal bones contain a good amount of CaO to be used as a catalyst for transesterification process. In this study, transesterification of Waste Frying Oil (WFO) with waste chicken bones as catalyst were studied. The effect of reaction condition such as reaction temperature, reaction time, molar ratio of methanol and oil and also catalyst concentration towards product yield were investigated. From the analysis results for the catalyst using XRD, SEM and FTIR, it shows that the waste chicken bones contain CaO that can be used as the catalyst for the transesterification process. For the effect of parameter studied, the result shows the yield of biodiesel increased with the increase of reaction temperature and the highest yield of 87.68% was obtained at reaction time of 3 h, reaction temperature of 60°C, catalyst concentration of 15% and molar ratio of methanol and oil is 6:1. From the chromatography peaks, it shows that the biodiesel consist of Methyl Laurate (C12:0), Methyl Myristate (C14:0), Methyl Palmitate (C16:0) and Methyl Palmitelaidate (C16:1). The highest compound contain in the product is Methyl Laurate (C12:0) with 56.54%.

Key words: Transesterification, waste frying oil, waste chicken bones, biodiesel, Malaysia

INTRODUCTION

Petroleum-based fuel becomes most energy needed over this century but it is limited and not sustainable. The low production and high pollution of natural petroleum nowadays result in the demanded of biodiesel derived from other sources such as edible and non-edible oil. Over 22 million tonnes of biodiesel was produced in Europe while United State (US) alone produced almost 3.7 million tonnes in 2011 (Nurfitri *et al*., 2013). It shows the demand for an alternative fossil fuel raised over the year because many of the research show the effective of biodiesel which can be derive from renewable and cheaper raw materials (Shomchoam and Yoosuk, 2014). The biodiesel that derive from pure oils are far more expensive than the nature diesel oil. Thus, waste frying oil is one of the alternative in producing biodiesel due to low raw materials cost. These waste frying oils may pose an environmental threat if they are not reused or disposed properly. Thus, it is necessary to take the advantage and opportunity to reduce at least 2-3 times of biodiesel production cost since the raw material cost has been cut down. The waste frying oils are sold at a cost 2-3 time lower than fresh or virgin feedstock and are often available free of cost (Guerra and Gude, 2014). Abundant of waste animal bones can be found especially in restaurant and wet market around Perlis. In fact, waste animal bones contribute huge number in our daily municipal waste. Most of these wastes are being thrown away without any proper treatment of disposal. Fortunately, it has ability to extract the mineral and it one of the sources for the heterogeneous catalyst. Those animal bones can react with methanol in order to produce Fatty Acid Methyl Ester (FAME). Because of these waste rarely used for other production, thus the huge number of raw material can be used in low cost. Most recent study stated that animal bones contain a good amount of CaO to be use in transesterification (Mahesh *et al*., 2015). In

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this study, transesterification of Waste Frying Oil (WFO) with waste animal bones as catalyst were studied. The effect of reaction condition such as reaction temperature, reaction time, molar ratio of methanol and oil and also catalyst concentration towards product yield were investigated.

MATERIALS AND METHODS

Pretreatment of Waste Frying Oil (WFO): The WFO sample was collected from restaurants around Padang Besar, Perlis and was filtered to remove impurities. Then, the WFO was treated by drying over calcium chloride ($CaCl_2$). The mixture was let to settle down overnight which results in accumulation of inorganic residue, $CaCl_2$ and water at the bottom of beaker. Next, the oil at the upper part (accumulation part was removed) was filtered to obtained more clear and clean oil before it can be further with transesterification process.

Preparation of waste chicken bone (catalyst) and analysis: The waste chicken bones was soaked in boiling water for 1 h and were rinsed with distilled water for 3 times before it was dried under sunlight for 2 day. After that, the bones were dried in the oven at 70°C for 24 h to remove the excess water. Dried bones were crushed using miller and had undergone calcination process in a furnace at 800°C for 3 h. Next, waste chicken bones had undergone analysis using Scanning Electron Microscope (SEM) (JSM-6490LV, Jeol) to determine the structure and morphology of the catalyst. On the other hand, the catalyst also had undergone X-Ray Diffraction (XRD) analysis by using model Shimadzu XRD-6000 to check the composition of CaO and Fourier Transform Infrared Spectroscopy (FTIR) to determine the functional group on the surface of the catalyst (Birla *et al*., 2012).

Transesterification process: About 50g of treated WFO were filled into 250 mL of 3-neck round bottom flask which equipped with a condenser and was heated using hot plate and agitated with magnetic stirrer. The methanol and catalyst was mixed at temperature of 40°C with constant stirred to activate the catalyst. After the treated oil reached the temperature of 50°C, the mixture of catalyst and methanol was added to the flask and the reaction take place for 3 h. After the reaction completed, the mixture was collected and then was filtered using filter paper to remove the catalyst. Then, the filtered mixture was loaded into rotary evaporator with temperature of 65°C. The rotary evaporator was used to remove the excess of methanol. The mixture then was placed in separating funnel to proceed to the purification step.

Four parameters were used such as reaction temperature, reaction time, ratio methanol to oil and concentration of catalyst. The temperature were varied from 40- 80, the molar ratio for methanol to oil were varied from 2:1-10:1, reaction time 1-4 h and concentration of catalyst from 5- 20%.

Purification steps: After the process of removing the excess methanol by rotary evaporator, the crude oil was transferred into separatory funnel and was left overnight. Two layer of mixture was formed and the upper layer known as methyl ester whilst the bottom layer known as glycerol. Then, the bottom layer (glycerol) was removed while the upper layer (methyl ester) was washed with the 50cm^3 of hot distilled water (50°C) contained three drops of ortho-phosphoric acid to eliminate the impurities and neutralize the pH. Lastly, the methyl ester was dried over anhydrous sodium sulfate beds twice to remove trace water. The pure FAME was weighted using balance and the result was recorded.

The FAME obtained from the process was analyzed using Gas Chromatography (GC) Model Shimadzu GC analyzer to determine the composition of the product yield. The GC was equipped with Flame-Ionization Detector (FID) and BP×70 capillary column (30 m length×0.25 μm thick×0.32 mm diameter) with temperature from 120-245°C at 4°C/min. The injector and detector temperature was at 245°C with nitrogen (20 cm min^{-1}) as carrier gas.

RESULTS AND DISCUSSION

Characterization of catalyst

XRD analysis: Figure 1 shows the patterns of XRD analysis for the waste chicken bones before and after calcination at 800°C for 3 h. Most of the CaO peaks were found in catalyst compound after the calcination process which is at the peaks of 32.3°, 37.3°, 58.3 and 64.1°. The number of CaO peaks increase after calcination process while the $CaCO_3$ and $Ca_5(PO_4)_3OH$ peaks were reduced which prove the transformation of $CaCO_3$ and $Ca_5(PO_4)_3OH$ into CaO that act as catalyst for transesterification process.

FTIR analysis: Table 1 shows the wavelength of each functional group that presence in the catalyst before and after calcination according to Fig. 2ab. The result in Fig. 2 ab shows absorbance band at 560.90cm^{-1} was belongs to Ca-O. This bond was strengthened by appearance of another bond at 876.04cm^{-1} which confirmed the conversion of $CaCO_3$ to CaO. The wide peak obtained at 1547.24 cm^{-1}, 1465.26 cm^{-1}, 1164.76 cm^{-1} and 1097.73 cm^{-1} before calcination process belongs to carbonate group (CO) from $CaCO_3$ compound which can be observed mostly before the calcination process while the O-C-O

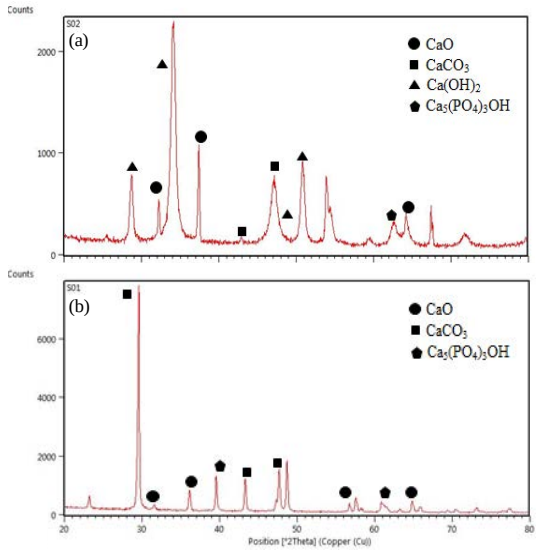

Fig. 1: The XRD pattern of waste chicken bones: a) Before calcination; b) After calcination at temperature of 800°C

Table 1: FTIR wavelength for each compound before and after calcination

	Wavelength (cm^{-1})	
Compound	Before calcination	After calcination
Ca-O	560.90	560.90
		876.04
C-O	1547.24	1097.73
	1465.26	
	1164.76	
	1097.73	
O-C-O	1745.00	
	1658.78	
P-C	2853.88	2924.99
	2924.99	
O-H	3413.57	3413.57

bond also from the CO group can be found at wavelength of 1745.00 and 1658.78 cm^{-1}. After the calcination process, these carbon groups reduce the intensity and same result has been reported (Lesbani *et al*., 2013) which shows most of CO group being release during calcination process. Besides, the OH- group from $Ca(OH)_2$ can be found at wavelength of 3413.57 cm^{-1} at waste chicken bones before the calcination process. Moreover, P-O bond from hydroxyapatite observed at peak of 2853.88 and 2924.99 cm^{-1} also at compound before calcination process. Both of these compounds had reduced their intensity showing that those compound had been remove during the calcination process at high temperature.

SEM analysis: Figure 3 a,b indicate the structure of waste chicken bones before and after the calcination respectively at magnification of 3000x. It clearly shows the

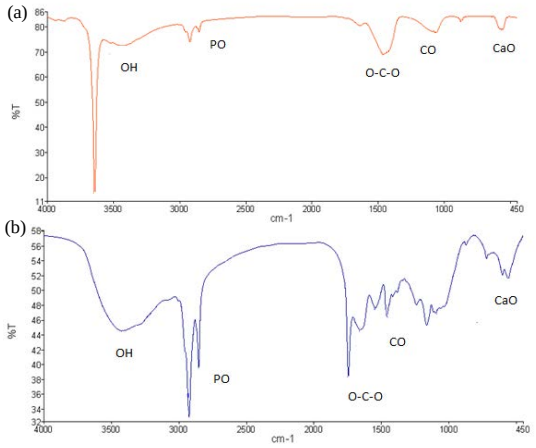

Fig. 2: FTIR spectrums for waste chicken bones: a) Before; b) After calcination process

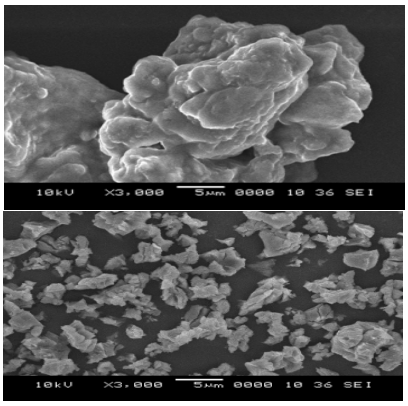

Fig. 3: SEM photograph for waste chicken bones before at 3000×magnification

difference in structure where the waste chicken bones before thermal decomposition was very bulky and had an irregular crystal shape compared to the structure of waste chicken bones after calcined which is more structured and in a crystal shape. In term of size, the waste chicken bone before calcination were around 20 μm in diameter while the size is reduce to around 5 µm in diameter after the calcination process. As the size reduces, particle became finer and they were closely connected together.

The size of particle is closely related to the total surface area which proved smaller size give a larger surface area. This result is due to decomposition of Calcium Carbonate ($CaCO_3$) into Calcium Oxide (CaO) and Carbon dioxide (CO_2) which reduce the particle size (Tan *et al*., 2015).

Effect of parametric study on the biodiesel yield

Reaction temperature: The effect of reaction temperature was investigated in the range of 50-80°C as shown in

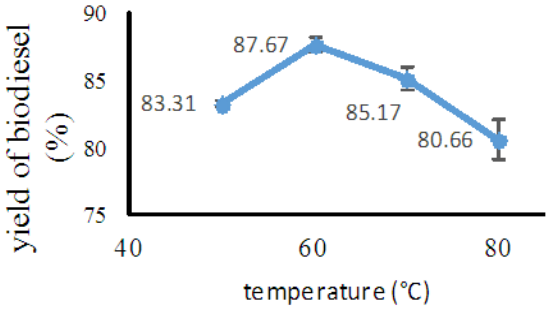

Fig. 4: Effect of reaction temperature on biodiesel yield using reaction time of 3 h, catalyst concentration of 15% and molar ratio of methanol and oil is 6:1

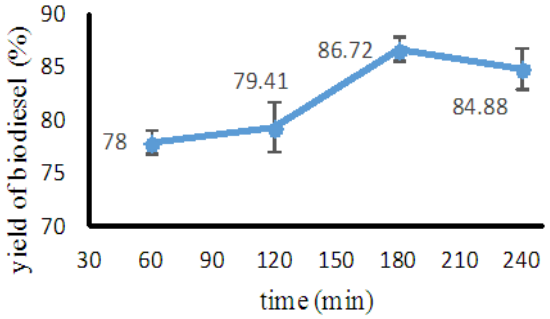

Fig. 5: Effect of reaction time on biodiesel yield using reaction temperature of 60°C, catalyst concentration of 15% and molar ratio of methanol and oil of 6:1

Fig. 4 while the other parameters such as reaction time, methanol to oil ratio and catalyst concentration was fixed at 3 h, 6:1 and 15% respectively. The result shows the yield of biodiesel increased with the increase of reaction temperature and the highest yield of 87.68% is recorded at 60°C. However, the yield of biodiesel reduces when the temperature of the reaction beyond 60°C where the lowest yield of 80.66% is recorded at 80°C. This is because the reaction temperature is over the boiling point of methanol (68°C) (Farooq *et al*., 2015). At this temperature, most of the methanol is vaporized and less oil will react with methanol to produce methyl ester (Hamamre and Yamin, 2014).

Reaction time: Figure 5 shows the effect of reaction time on the yield of biodiesel. The time is manipulated from 1-4 h while the other parameters are kept constant at 60°C, 6:1 and 15% for reaction time, methanol to oil ratio and catalyst concentration respectively. The graph shows that the yield of biodiesel was increased with the increased of reaction time. The optimum reaction time was at 180 min as the yield produce was the highest which is about 86.72%. At this time, most of the oil is converted to methyl ester by methanol and catalyst. Further reaction

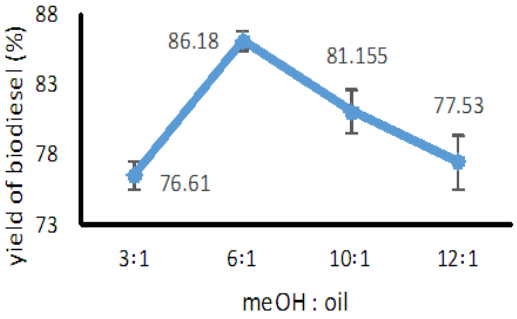

Fig. 6: Effect of methanol to oil ratio on biodiesel yield using reaction temperature of 60°C, catalyst concentration of 15% and reaction time of 3 h

time beyond 3 h results in decreased of biodiesel yield. By using the optimum temperature of 60°C for the reaction, it can be consider really close to boiling point of methanol which can cause large volume of methanol loss as longer reaction time is used (Mahesh *et al*., 2015). Thus, fewer methanol can be remained to convert oil to methyl ester. Moreover, saponification also happened which lower the yield of biodiesel produce at 240 min with 84.88% yield.

Molar ratio of methanol to oil: Figure 6 shows the effect of molar ratio of methanol to oil on the yield of biodiesel. The molar ratio of methanol to oil was varied from 3:1-12:1 while other parameters were fixed: reaction temperature at 60°C, reaction time at 3 h and the catalyst concentration at 15%. The highest yield of 86.18% was recorded when the methanol to oil ratio at 6:1. At this stage, the optimum amount of methanol shifts the reaction to the right which increases the yield of biodiesel (Hasuntree *et al*., 2011). While the lowest yield of biodiesel of 76.62% was obtained at first methanol to oil ratio (3:1) as the amount of methanol is to low and not enough to convert more triglycerides to methyl ester and glycerol (Lam *et al*., 2010).

Catalyst concentration: To investigate the effect of catalyst concentration on the production yield of biodiesel, the study was carried out using catalyst concentration in the range of 5-20% as shown in Fig. 7. The other parameters are kept constant such that the reaction temperature, reaction time and methanol to oil ratio were at 60°C, 3 h and 6:1, respectively. The result clearly shows that the yield of biodiesel was increased with the increased of the catalyst concentration. By using 5 and 10%, the production of biodiesel were about 76.82 and 82.42%, respectively.

But, the highest amount of biodiesel (86.50%) were obtained by using 15% of catalyst concentration which indicate the optimum amount of catalyst concentration for

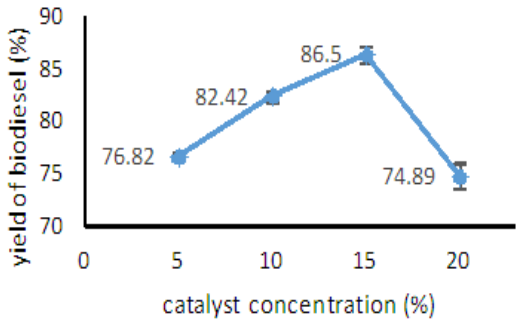

Fig. 7: Effect of catalyst concentration on biodiesel yield using reaction temperature of 60°C, reaction time of 3 h and methanol to oil ratio of 6:1

Table 2: Compound identified in biodiesel sample by GC

Peaks	Retention time	Compound	Common name	Compound (%)
1	10.001	C12:0	Methyl Laurate	56.54
2	13.111	C14:0	Methyl Myristate	2.09
3	13.563	C16:0	Methyl Palmitate	33.48
4	14.416	C16:1	Methyl Palmitelaidate	7.89
Total FAME	100			

the transesterification process of WFO using waste chicken bone as catalyst. However, as the concentration of catalyst is keep increasing to 20% which is over the optimum value, the yield of biodiesel sharply reduces to 74.89%. When the large amounts of catalyst were present in excess, the mixture become too viscous and lead to formation of soap. Thus, the separation process during purification become difficult and completely reduces the yield of biodiesel (Georgogianni *et al*., 2009).

GC analysis: Table 2 shows the compound that presence in the biodiesel yield. There were four compound identified in the product which are Methyl Laurate (C12:0), Methyl Myristate (C14:0), Methyl Palmitate (C16:0) and Methyl Palmitelaidate (C16:1). From Table 2, C12:0 contain the highest portion in the product with 56.54% followed by C16:0 with 33.48%. In other hand, small portion of C14:0 and C16:1 also contained in the product about 2.09 and 7.89% respectively. This result shows the product contain both saturated and unsaturated fatty acid such as C14:1. With the present of FAME in the product, thus prove that the transesterification of WFO over waste chicken bones produced biodiesel with high percentage of FAME.

CONCLUSION

The analysis of the catalyst by using XRD, it shows that the waste chicken bones contain CaO that can be used as the catalyst for the transesterification process. With the result obtained by FTIR, it proved that the waste chicken bones can be used as catalyst in transesterification process as most of CO group and OH group had been remove and results in CaO compound. For the effect of parameter studied, the result shows the yield of biodiesel increased with the increase of reaction temperature and the highest yield of 87.68% was obtained at reaction time of 3 h, reaction temperature of 60°C, catalyst concentration of 15% and molar ratio of methanol and oil is 6:1. From the chromatography peaks, it shows that the biodiesel consist of Methyl Laurate (C12:0), Methyl Myristate (C14:0), Methyl Palmitate (C16:0) and Methyl Palmitelaidate (C16:1). The highest compound contain in the product is Methyl Laurate (C12:0) with 56.54%.

ACKNOWLEDGEMENTS

The researchers would like to pay appreciation to Ministry of Higher Education under Fundamental Research Grant Scheme (FRGS) No. 9003-00382 for the financial support and Universiti Malaysia Perlis for the facilities provided.

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