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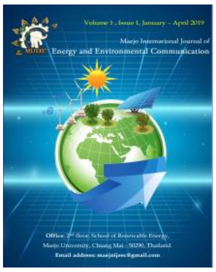

ARTICLE

Mixed domestic-waste catalysts for methyl ester production of soybean oil

Siti Norhafiza Mohd Khazaai[1,2], Nurul Aina Nasriqah Ma'arof [1], Nurul Hajar Embong[1], Mohd Hasbi Ab. Rahim[1], Gaanty Pragas Maniam[1,3,*]

[1]Faculty of Industrial Sciences & Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia.
[2]Faculty of Applied Sciences, Universiti Teknologi MARA Pahang, Jengka, Pahang, Malaysia.
[3]Central Laboratory, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia.

*Corresponding author, *E-mail address*: gaanty@hotmail.com

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ABSTRACT

Nowadays due to the depletion of non-renewable energy resources, production of green material from domestic wastes has played an important role. The waste of banana peel impregnated with calcium oxide (CaO) from eggshell had successfully been used as a low-cost catalyst to transesterify soybean oil to produce methyl ester. The catalytic actions from potassium and calcium oxide content in calcined banana peel (700°C) and eggshell (900°C) discover through FT-IR, XRD, and SEM. Methyl ester conversion can be obtained at 76.87 wt.% with the optimal condition of 7 wt.% of catalyst amount, methanol/oil mass ratio, 9:1; and the reaction temperature, 65 °C within 2 h reaction time.

1. Introduction

Biodiesel, an environmental-friendly alternative energy source (Lund et al., 2014; Unpaprom et al., 2015) continues growing due to the shortage of fossil resources and significant concern with regard to environmental conservation. In addition, some countries like the United State and the European Union implement an energy policy that requires transportation sector to use more biodiesel have also contributed to the demand for biodiesel. Biodiesel is compatible with conventional diesel even contains no petroleum products and can be blended with petroleum diesel in any proportion to create a more stable biodiesel blend.

Transesterification is the most well-known process to produce biodiesel which involves the conversion of component triglycerides to a mixture of fatty acids alkyl esters and glycerol with short chain alcohols like methanol and ethanol (Unpaprom et al., 2015; Ramaraj et al., 2016). Commonly, the transesterification process is favored with the aid of a catalyst. The presence of a catalyst (typically a strong acid or base) accelerates considerably the adjustment of the equilibrium. Transesterification is the best suit process to lower the viscosity and at the same time increase the volatility of the oil. It has been proven that the conversion of oil to methyl esters, with a suitable catalyst, reduce the molecular weight up to 66 %. To date, the cost of the biodiesel production is the serious challenge on its large-scale commercialization. Therefore, high-efficiency and cost-effective catalysts are highly desirable for transesterification. In this regards, the exploitation of waste materials for the production of biodiesel could be the elegant path to make the process economically.

Recently, the researchers have a great attention to use and develop heterogeneous catalyst from waste resources such as biomass, eggshell and nanoporous material as an attempt to reduce the cost (Bennet et al., 2016; Shan et al., 2016; Abdulah et al., 2017). In this study, waste of banana peel is used as a source of potassium carbonate (K_2CO_3). The banana fruit is abundantly available especially in Malaysia as it is the superb fruit that can give us energy, make us feel full and provide our body with essential nutrients (proteins, carbohydrates, phosphorus, vitamin A, iron, and potassium) and high amount of fibers. About 530,000 metric tonnes total production of banana were planted in Malaysia for local consumption by small farmers, and about 12% of it is exported especially to Singapore, Brunei, Hong Kong, and the Middle East (Sapuan et al., 2018).

As such, the more banana consumption, the more peels will dump to the landslide. Therefore, the banana peel is plentiful enough to be used. The catalytic compounds (K_2CO_3) from banana peel will impregnate with CaO also from waste sources (eggshell). Chicken eggshell has been evaluated as an effective catalyst to transesterify the triglyceride into methyl esters (Wei et al., 2009; Sharma et al., 2010; Chavan et al., 2015; Tan et al., 2015). The eggshell containing calcium carbonate (94%), calcium phosphate (1%), organic compounds (4%), and magnesium carbonate (1%) (Mohadi et al., 2016). An exothermic reaction takes place in the eggshell were contained a high amount of calcium carbonate that can be converted as a CaO catalyst during the calcination process at a temperature around 800°C for 2 h.

2. Materials and methods

Soybean oil used in this study as a feedstock was purchased at the nearby supermarket in Kuantan, Pahang. The banana peels and eggshell were collected from nearby stalls and restaurant in Kuantan, Pahang before used as a catalyst in the production of methyl ester. An analytical grade of methanol, n-hexane, n-heptane, petroleum ether, and chloroform were obtained from Merck. An analytical grade of methyl heptadecanoate, phenolphthalein, 4-nitroaniline and 2,4-dinitroaniline were purchased from Sigma Aldrich company (Switzerland).

Nomenclature and Abbreviation

K_2CO_3	Potassium carbonate
C_aO	Calcium oxide
FT-IR	Fourier transform infrared spectrometer
XRD	X-ray diffractometry
SEM	Scanning electron microscopy

2.1 Preparation of Catalyst

The collected waste of banana peels and eggshell were thoroughly washed with tap water to remove dirt and organic matter. The banana peels were dried in the oven about 80 h at temperature 100˚C while the eggshell was dried for 24 h at a temperature of 105˚C. Then, the dried banana peels and eggshell were powdered separately using a grinder. The banana peels powder was calcined in a furnace at 700 °C for 4 h and the eggshell powder was calcined at 900 ˚C for 3 h. The calcined banana peels and eggshell were assigned as CBP and CES respectively. The CES was impregnated to CBP with different concentrations (10 wt. %, 20 wt. %, 30 wt. %, and 40 wt. % in order to get the desired catalyst, CaO-K_2CO_3. The CaO-K_2CO_3 catalyst was analyzed via Fourier Transform Infrared (FTIR) spectrophotometer, Brunauer-Emmett-Teller (BET) analysis, Thermogravimetric analysis (TGA) and Field Emission Scanning Electron Microscopy (FE-SEM). The basic strength of the catalyst was tested using Hammett indicators; phenolphthalein (H_ = 8.2), 2, 4-dinitroaniline (H_= 5), 4-nitroaniline (H_=8.4).

2.2 Reaction process

The transesterification of soybean oil and methanol were carried out in a 50 ml one-neck round bottom flask with a magnetic stirrer, condenser, and thermometer, immersing in a water bath. The reaction process was controlled at a temperature of 65 ± 2 °C. Several reaction parameters (catalyst amount, reaction hours and the molar ratio of methanol to oil) were studied to identify the optimum reaction conditions needed. The product solution was allowed to cool so that the glycerol can be separated by gravity. Centrifugation was used to further separate the products and by product layers to obtain pure methyl esters.

2.3 Gas chromatography analysis

The GC-FID with a capillary column of HP-INNOWAX (length 30 m x internal diameter 0.25 mm x film thickness 0.25 μm) was used to determine the conversion of methyl ester produced. Methyl heptadecanoate was used as an internal standard. The methyl ester conversion was determined following the European regulation procedure EN 14103 by comparing the identified methyl ester peaks with respective internal standard.

3. Results and discussion

The acid value, moisture content, iodine value, density and a saponification value of the oil were tabulated in Table 1. The low FFA value (0.5 %), equivalent to the acid value of soybean oil possibly achieved the circumstance of the alkaline route in the transesterification reaction. Fortunately, the moisture content in this oil was found to be 0.12 % may reduce the possibility for the formation of soap through hydrolysis reaction of triglyceride via the changes of Lewis site of base catalyst into Bronsted base catalyst (Luque et al., 2012).

Table 1. Characterization of soybean oil

Parameters	**Present work**	**(Hasan et al., 2016)**	**(Kady et al., 1993)**
Acid value, mg KOH/g	1.01	0.36	0.88
Moisture content, %	0.12	0.31	-
Iodine value, mg I_2/g	64.7	105.47	124.56
Density, g/cm^3	0.9163	0.909	-
Saponification value, mg KOH/g	202.52	184.8	190.5

FTIR analysis was used to identify the functional groups present in the catalyst. UCBP, CBP, and CaO-CBP were analyzed in order to view the differences. In the spectrum of UCBP, the broad peak which located at the wavenumber 3447.11 cm^{-1} indicated the O-H bonds stretching vibration. The peak for C-O stretch showed at 1049.83 cm^{-1} and 1653.00 cm^{-1}. The peak at 1506.50 cm^{-1} referred to N-O stretching while 1384.58 cm^{-1} assigned to carbonate C-O stretching and bending vibrations. 667.71 cm^{-1} indicated to C=C bending for alkene. For the spectrum of CBP, the bands at 3436.03 cm^{-1} were appeared due to O-H stretching and bending vibrations of H_2O while the other bands at 1630.94 and 1384.26 cm^{-1} assigned to carbonate C-O stretching and bending vibrations, which were indicative of the presence of carbonate (CO_3). Aransiola et al. (2010) stated that the characteristic band at 1384.26 cm^{-1} was referred to K_2CO_3 and prominent only in the calcined sample (CBP and CaO-CBP). At the peak of 1461.82 cm^{-1} and 669.04 cm^{-1} indicated C-H bending and C=C bending, respectively. Meanwhile, for CaO-CBP spectrum, the absorption band at 3420.60 cm$^{−1}$ that could be ascribed as OH stretching bands. The bands at 1460.01cm$^{−1}$ and 869.48 cm$^{−1}$ in this spectrum correspond to the C–O bond. The wide and strong bands at around 569.58 cm$^{−1}$ corresponded to Ca–O bonds. The FTIR peak position at 3643.97 cm$^{−1}$ indicated the presence of an isolated hydroxyl group (OH). This isolated OH group becomes responsible for active catalytic activity (Sahu et al., 2017). The peak of 1048.90 cm^{-1} indicated as strong C-O stretching while 1627.25 cm^{-1} referred as medium C=C stretching of alkene and C-H bending for aldehyde was shown at 1384.51 cm^{-1}. Throughout the FTIR results, it shows that the impregnation of CaO on CBP was done successfully. The surface area and pore volume of UCBP, CBP, and CaO-CBP were analyzed by using BET. The surface area is increased from UCBP (4.8529 m^2/g) to CaO-CBP (23.0722 m^2/g). Meanwhile, for UCBP (0.0031 cm^3/g, 25.8222 cm^3/g) to CBP (0.0205 cm^3/g, 51.3117 cm^3/g), increasing value were observed for the pore volume and pore size but against observation for CBP to CaO-CBP (0.0191 cm^3/g, 33.1211 cm^3/g).

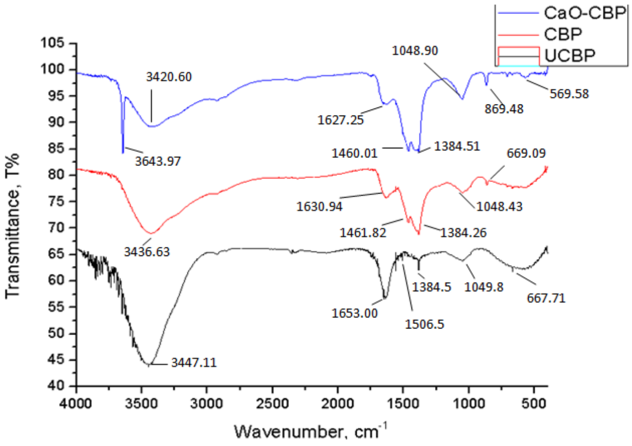

Figure 1. FTIR spectra of UCBP, CBP, and CaO-CBP

The alteration obviously occurred after undergo the calcination process and impregnation method with CaO compound. The pore size also increased from 25.8222 Å to 51.3117 Å, and then decreased to 33.1211 Å. During calcination process, the increased of surface area with loading amount of CaO may be due to the much higher pore volume or opening of closed pores on the surface of the catalyst during calcinations (Sahu et al., 2017). The H_ values of the CaO-CBP catalyst were determined by using Hammett indicators. The observation reveals the pH range of CaO-CBP catalyst was higher than 9.8 in phenolphthalein indicator due to changing color from colorless to pink but unchanged color for the 2,4-dinitroaniline and 4-nitroaniline (Joshi et al., 2015). This shows that it had basicity in the range of 9.8 < H_ < 15.0, indicated a moderate base strength and expected to be the catalytic promoter in the transesterification reaction.

The surface morphologies with EDX for elemental composition of the UCBP, CBP and CaO-CBP catalysts was studied by scanning electron microscopy (SEM) and the images obtained were very irregular in shape are shown in

Figure 2 (a), (b) and (c) respectively. According to Figure 2(a), it can be clearly observed that the UCBP is in highly irregular and clustered form. Uncalcined material was not able to give high conversion efficiency due to less active surface availability (Sahani et al., 2018). Concurrently, CBP surface showed the nodule like appearance with quite a rough surface where the agglomerated particles are uniformly distributed throughout the irregular-shaped flat surface of the developed catalyst after calcination at 900 °C for 3 h. However, the surfaces of metal impregnated catalysts in Figure 2(c), generally had the formation of smaller aggregates of variable morphologies throughout the catalysts. The formation of clusters of CaO-K_2CO_3 particles would lead to the irregularities in the morphologies of metal impregnated catalysts during their impregnation method preparation (Aransiola et al., 2010). The smaller the size of aggregates could provide the higher specific surface areas. In this study, the CBP catalysts were synthesized with a varied amount of CaO concentration revealed the best optimal percentage of 30 wt% with 93.31 % methyl ester conversion. The active site (basic site) had increased as the total basicity of CaO concentration increase from 10 % to 30 % in transesterification reaction (Irmawati et al., 2014). Unfortunately, methyl ester conversion slowly reduced when the increasing CaO concentration due to the crystallization and agglomeration on the excessive active species at the surface of a catalyst which leads to poor dispersion of CBP species. Figure 3(b) showed the average methyl ester conversion involving reaction hour's parameter with the optimal condition was 82.29 % at 2 h reaction. The maximum yield of ME conversion can be reached at a short time as the interaction of oil and methanol fast. But the methyl ester conversion would remain constant when reached the equilibrium condition (Talha and Sulaiman, 2016). However, when exceeds the optimum reaction time, the unwanted reactions such as saponification (soaps formation) would occur and decrease the FAME yield production. Methanol to oil molar ratio was one of the parameters used in the optimization of methyl ester yield. The conversion of methyl ester was investigated at 6:1 to 15:1 of methanol to oil molar ratio with 7wt. % catalyst amount within 2 h of reaction hours. The methyl ester conversion was increased from 44.79 % to 82.29 % when the amount of methanol to oil ratio increased from 6:1 to 9:1, nevertheless, when the methanol to oil molar ratio beyond to the optimum value, the conversion slowly decreased to 64.60 % and 46.71 % respectively. In transesterification reaction, the excess amount of alcohol used would lead to the increased solubility of glycerine and causing the difficulties in separation of biodiesel and glycerol, especially under high temperature (Basumatary, 2014). The catalyst used in the reaction will play an important role in affecting the yield of FAME synthesized by speed up a reaction by lowering the activation energy of the reaction. In this research study, 30 wt. % CaO-CBP was used as the catalyst throughout the transesterification reaction.

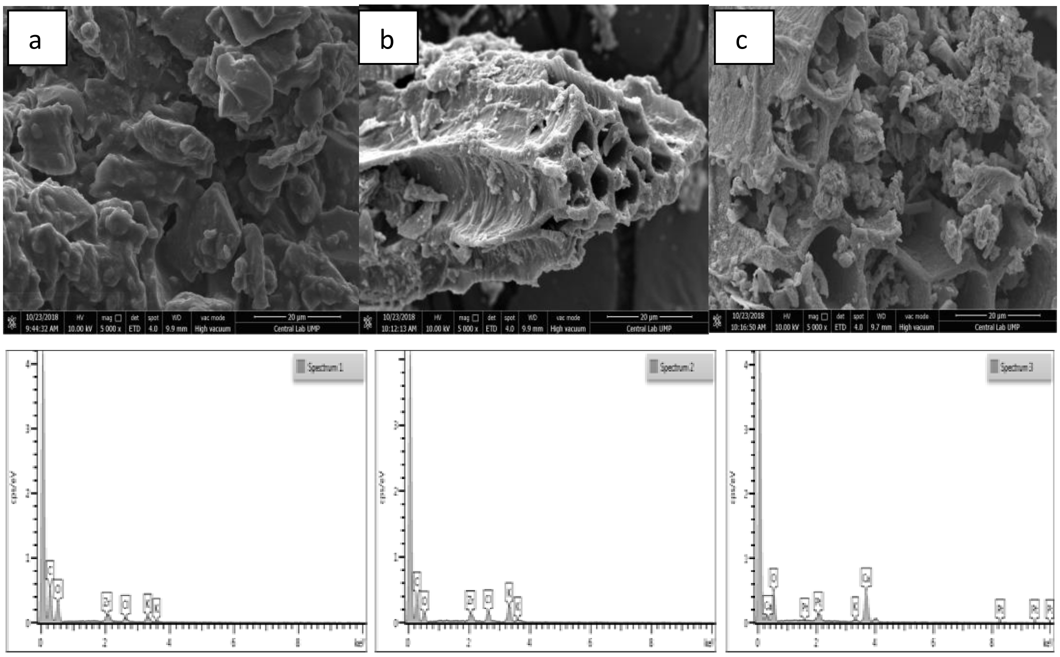

Figure 2. SEM-EDX micrographs of a) UCBP, (b) CBP, and (c) CaO-CBP

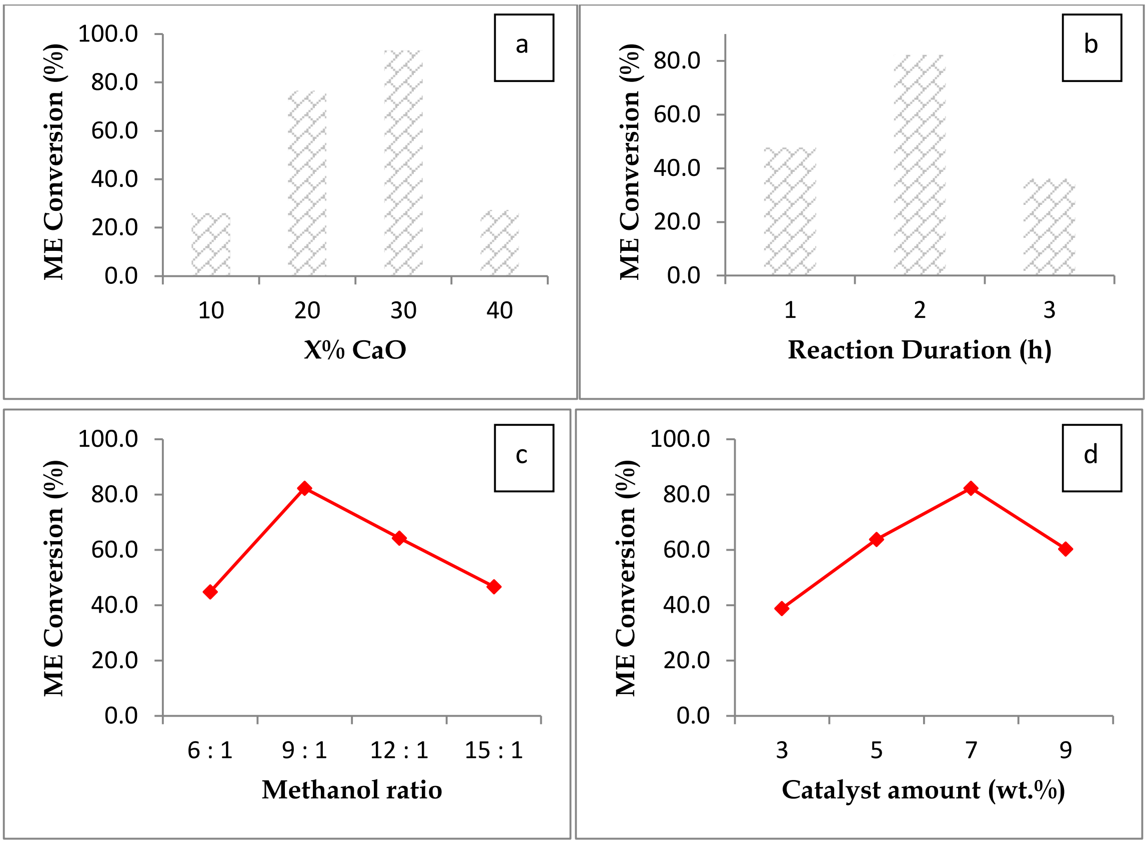

Figure 3. Effect of (a) CaO loading, (b) reaction duration, (c) methanol/oil molar ratio, and (d) catalyst amount on the methyl ester conversion

The catalyst amount varied from 3 wt. % to 9 wt. % based on the weight of soybean oil. Methyl ester conversion increased from 38.78 %, 63.85 % to 82.29 % at 7 wt. % of the catalyst. As the amount of catalyst increased, the methyl ester conversion was gradually increased due to the increases of the active site for reactant to undergo reaction. However, the methyl ester conversion decreased to 60.32 % when the amount of catalyst used increased to 9 wt. %. After all, all the reaction parameters involved significantly have to achieve the best optimal condition to obtain a high methyl ester conversion.

Conclusion

As a summary, the CaO-K_2O_3 catalyst was capable of enhancing the catalytic performances of both single metal oxides (eggshell (CaO) and banana peel (K_2O_3)). The impregnation of both single metal oxides able to enhance the catalytic performance in the transesterification reaction. Certify the catalyst capable of yielding 82.29 % of methyl ester in 2 h of reaction time at 65 °C with MeOH/oil mass ratio, 9:1; catalyst amount, 7 wt%. The use of this type of catalyst may offer a cost-efficient and eco-friendly alternative to the existing catalyst for biodiesel production.

Acknowledgments

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