Biodiesel production from waste cooking palm oil using calcium oxide supported on activated carbon as catalyst in a fixed bed reactor

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Abstract−A reactor has been developed to produce high quality fatty acid methyl esters (FAME) from waste cooking palm oil (WCO). Continuous transesterification of free fatty acids (FFA) from acidified oil with methanol was carried out using a calcium oxide supported on activated carbon (CaO/AC) as a heterogeneous solid-base catalyst. CaO/AC was prepared according to the conventional incipient-wetness impregnation of aqueous solutions of calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$) precursors on an activated carbon support from palm shell in a fixed bed reactor with an external diameter of 60 mm and a height of 345 mm. Methanol/oil molar ratio, feed flow rate, catalyst bed height and reaction temperature were evaluated to obtain optimum reaction conditions. The results showed that the FFA conversion increased with increases in alcohol/oil molar ratio, catalyst bed height and temperature, whereas decreased with flow rate and initial water content in feedstock increase. The yield of FAME achieved 94% at the reaction temperature 60 °C, methanol/oil molar ratio of 25 : 1 and residence time of 8 h. The physical and chemical properties of the produced methyl ester were determined and compared with the standard specifications. The characteristics of the product under the optimum condition were within the ASTM standard. High quality waste cooking palm oil methyl ester was produced by combination of heterogeneous alkali transesterification and separation processes in a fixed bed reactor. In sum, activated carbon shows potential for transesterification of FFA.

Key words: Biodiesel, Waste Cooking Palm Oil, Heterogeneous Catalysis, Fixed Bed Reactor

INTRODUCTION

Biodiesel produced from vegetable oil and animal fats provides a good alternative to fossil fuel [1]. The cetane number, flash point, and lubricity of biodiesel are better than those of petroleum diesel [2]. Biodiesel sources do not contain significant amounts of nitrogen and sulfur compounds. Therefore, it has lesser amounts of NO_x and SO_x polluting emissions and is much cleaner than petroleum diesel fuel. The simple alkyl esters of fatty acids, derived from oils, also have uses other than as an energy source, such as in foods, textiles, cosmetics, rubber, and synthetic lubricant industries. The fatty acid methyl ester (FAME) is predominantly used as biodiesel [3]. However, biodiesel has currently not been commercialized worldwide because of the high cost of feedstock oil [4]. One alternative way to reduce the cost of biodiesel production is to employ waste oils such as cheap deodorizer distillates available from the refining of vegetable oils [5,6] or waste cooking oil (WCO), originating from restaurants and household disposals. Due to the presence of considerable free fatty acid (FFA) in such feedstock, the alkaline homogeneous catalyzed process is not recommended. Because a large amount of soap byproduct is formed during the reaction, the basic alkaline process creates serious problem of product separation and ultimately lowers the yield substantially [7,8]. Although the homogeneous acid catalyzed process can be employed to produce biodie-

sel, this process is operated at high temperature and gives rise to serious environmental and corrosion problems. In addition, the homogeneous acid catalyst is difficult to recycle as a result of high cost production [9,10].

The increasing production of WCO from household and industrial sources is a growing problem all around the world. This residue is regularly poured down the drain, resulting in problems for wastewater treatment plants and energy loss, or is integrated into the food chain through animal feeding, thus becoming a potential cause of human health problems [11]. There are several end-uses for this waste, such as the production of soaps or of energy by anaerobic digestion, thermal cracking [12], and more recently the production of biodiesel, a fuel that can be used as a mineral diesel substitute for engines. The core process of the biodiesel production consists in the transesterification of the raw materials, vegetable oils and fats, using a short chain alcohol.

In this study, we developed a fixed bed reactor system for transesterification of waste cooking palm oil. The work was focused on the reaction parameters that affected calcium oxide supported on palm shell activated carbon (CaO/AC) solid-catalyzed transesterification of WCO with methanol in a continuously fixed bed reactor. Among the available supports, activated carbon has proved to be a highly effective catalyst support in liquid and vapor phase reactions such as heterogeneous transesterification reaction [13]. Its high specific surface area, inert carbon skeleton and controllable pore structure allow catalyst to disperse over it largely and effectively. In addition, it is stable in high pressure and temperature reaction condi-

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Table 1. Physicochemical properties of waste cooking palm oil feedstock

Properties	Waste cooking palm oil
Density (g/ml, 15 °C)	0.868
Relative molecular weight	900.0
Saponification value (mg KOH/g oil)	156.60
Acid value (mg KOH/g oil)	97.03
Free fatty acid (%)	40.98
Water content (%)	0.10
Impurity (%)	3.00

tions [14,15]. Our objectives were to better understand the relationships between the reaction variables (methanol/oil molar ratio, feed flow rate, catalyst bed height and reaction temperature) and the response, FAME yield (wt%) and to achieve the optimal continuous transesterification condition in a fixed bed reactor system.

EXPERIMENTAL SECTION

1. Materials

WCO containing 40.98 wt% FFA and 0.10 wt% water was collected in university cafeterias and local restaurants. The numerous fractions were blended in order to obtain waste oil. The basic properties of oil are shown in Table 1. Non-oil components of the WCO were removed by separation. Filter paper with an average pore size of 5 mm was used to remove impurities from the oil feedstock before use. The activated carbon (1-2 mm particle size) used in this work was palm shell-based, produced by physical activation process. All other chemicals were analytical grade reagents (Merck, >99% purity) and were used as received.

2. Catalyst Preparation

Supported metal oxide catalysts were prepared according to the conventional incipient-wetness impregnation of aqueous solutions of the corresponding $Ca(NO_3)_2 \cdot 4H_2O$ precursors on an activated carbon support. Calcium nitrate salt was completely dissolved in deionized water at room temperature. Amount of metal loading was maintained at 20 mmol metal/g support. The support was then added

into the solution followed by vigorous mixing. After mixing for 4 h, the paste was dried in an oven at 120 °C overnight. The dried solid was calcined at 600 °C for 4 h. The characterization of these synthesized catalysts has been reported in our previous publication [16].

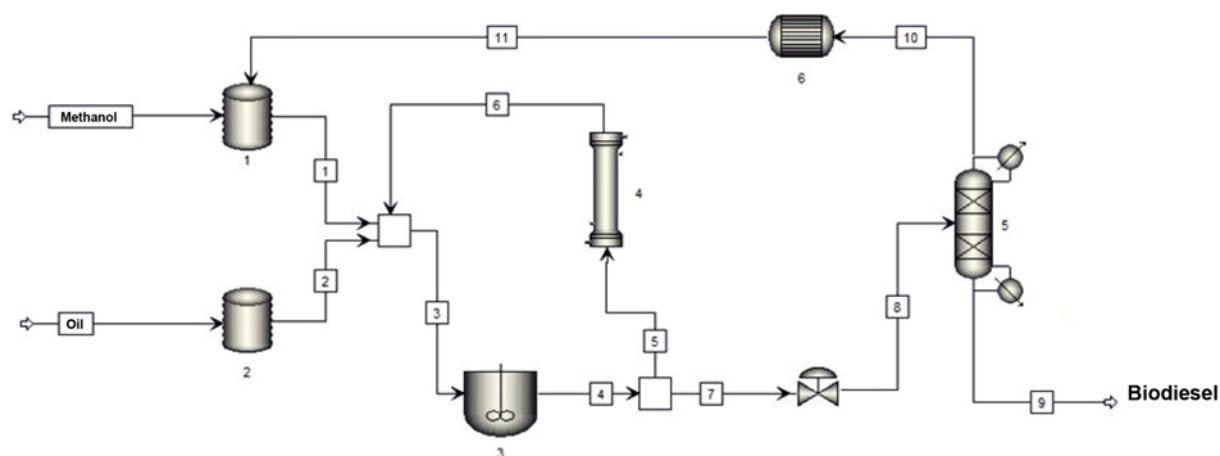### 3. Continuous Transesterification in a Fixed Bed Reactor

The continuous transesterification was performed in a fixed bed reactor. The scheme of the fixed bed reactor was shown in Fig. 1. The reactor was composed of a water-jacketed stainless steel column with an external diameter of 60 mm and a height of 345 mm. The column was packed with palm shell activated carbon supported calcium oxide solid-base catalyst. Waste cooking palm oil and methanol were charged into the system by using two separate raw material pumps. WCO and methanol were mixed and preheated in a mixing tank. The reactant was fed to the inlet of reactor with a pump. The reaction temperature was controlled by a heater to keep constant temperature with an error of ±1.0 °C. The temperature difference between the inlet and the outlet was below 1.0 °C during all the runs. Temperature and pressure of the system were monitored by temperature indicator and pressure gauges. The sample obtained was purified by reduced pressure distillation to remove the excess methanol and water generated during reaction. The conversion (%) of FFA in the WCO into biodiesel was calculated from the mean of acid value (AV) of the oil layer [17,18] by the following Eq. (1).

$$\text{Conversion (\%)} = \left(1 - \frac{AV_{OL}}{AV_{WCO}}\right) \times 100 \qquad (1)$$

Crude biodiesel (CB) was taken to analyze the purity by gas chromatography-mass spectrometry (GC-MS) (Varian CP-3800). Purity of crude biodiesel refers to the conversion of WCO into biodiesel in each performance. The purity (%) of crude biodiesel was calculated based on the area (A) of biodiesel over the reference (R) and the weight (W) of reference over the crude biodiesel [19] by the following equation:

$$\text{Purity (\%)} = \frac{A_{FAME}/A_R \times W_R}{W_{CB}} \qquad (2)$$

Methanol is one of the essential reactants in the transesterification; it is necessary to recycle and return it to the process. For this

Fig. 1. Schematic diagram of continuous reactor to produce biodiesel.
    1. Methanol tank   2. Feedstock oil tank   3. Mixing tank   4. Fixed bed reactor   5. Separator   6. Condenser

purpose a simple and effective methanol recovery unit was employed. The methanol recovery unit, which is based on continuous distillation, consists of a condenser and a heater. The permeate stream containing biodiesel, methanol and glycerol was collected in the separator. The high temperature leads to methanol evaporation, immediately. Methanol, which has a lower boiling point, was continuously evaporated, distilled and returned to the system to minimize its consumption. Most biodiesel production processes use excess methanol to get high yield. Excess un-reacted methanol can be separated and recycled easily by vaporization after reaction, but high energy is generally required. For a cost-effective methanol recycle, an efficient design is needed to subsidize the high energy requirement. Some biodiesel manufacturers are now using distillation column and flash evaporation for methanol recycles [20].

RESULTS AND DISCUSSION

1. Effect of Process Parameters

In the fixed bed reactor, under the conditions of reaction temperature of 60 °C, methanol/oil ratio of 25 : 1 and catalyst bed height 295 mm, the pretreatment on the waste cooking palm oil was performed. Changing the flow rate of feedstock oil, different residence time was obtained. The corresponding transesterification conversion with the residence time is shown in Fig. 2. The acid value was reduced from 97.03 mg KOH/g to 1.28 mg KOH/g when the residence time was as long as 7 h. However, from the 7th hour to the 8th hour, the acid value only decreased a little. This can be explained by that transesterification reaction between WCO and methanol is reversible; when the reaction time is long enough, the hydrolysis reaction of fatty acid ester will strengthen to generate more fatty acid ester and water. This causes the acid value to reduce with much resistance when it is at a relatively low value. Thus, from an economical point of view, it is not necessary to spend a long time to decrease the acid value of acidified oil, such as below 1 mg KOH/g, when the acid value has been reduced enough to avoid saponification in the transesterification reaction. [21].

Methanol and oil are immiscible. Usually, a high methanol/oil ratio improves the oil dispersion under agitation; thus the transesterification can be easily performed. High methanol/oil ratio also favors increase in yield of valuable oil. Excess un-reacted methanol can be recycled easily by vaporization after reaction. The effect
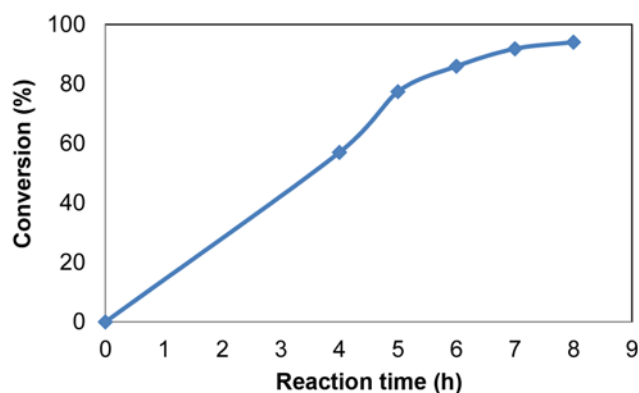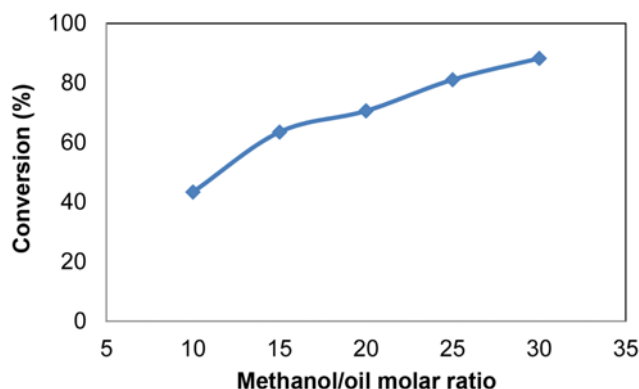
Fig. 3. Effect of methanol/oil molar ratio on the conversion of transesterification in the fixed bed reactor.

of methanol/oil ratio was investigated from 10 : 1 to 30 : 1. Fig. 3 lists the methyl ester yields for the various molar ratios of methanol/oil at a flow rate of 1 ml/min at 60 °C in the fixed bed reactor, which was filled with palm shell activated carbon supported calcium oxide solid-base catalyst. The initial increment from 10 : 1 to 15 : 1 gave a one-fold increase in yield of transesterification (43.38-63.51%). The viscosity of WCO is reduced on the increase in methanol amount. According to Le Chatelier's principle, the increase in methanol amount was responsible for the reduction in backward reaction and increased product yield [22,23]. The increase in transesterification became slower upon further increase in methanol/oil 15 : 1 and 25 : 1 ratio and leveled off at 25 : 1 to 30 : 1 methanol/oil ratio (yield 81.10-88.25%). Consequently, the methanol/oil ratio of 25 : 1 was further studied in the transesterification of waste cooking palm oil under our experimental conditions. It can be seen that our transesterification system uses a relatively large amount of methanol. This increased methanol requirement could be explained by the observation above that the calcined Ca(NO$_3$)$_2$/AC exhibited a real heterogeneous catalysis in which the mass transfer between the immiscible liquid phases and the solid catalyst surface is a major limitation. The larger amount of methanol would then facilitate the diffusion of reactants and the formation of active methoxide species, resulting in a higher methyl ester content [24].

The effect of temperature on the conversion of oil to methyl ester was studied by varying the temperature from 40 to 70 °C and keeping fixed the 25 : 1 methanol/oil molar ratio with 1 ml/min flow.
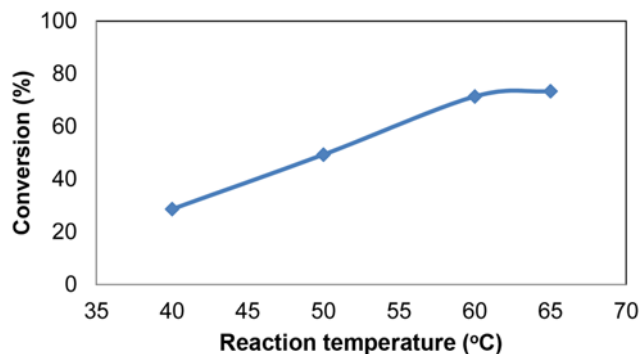
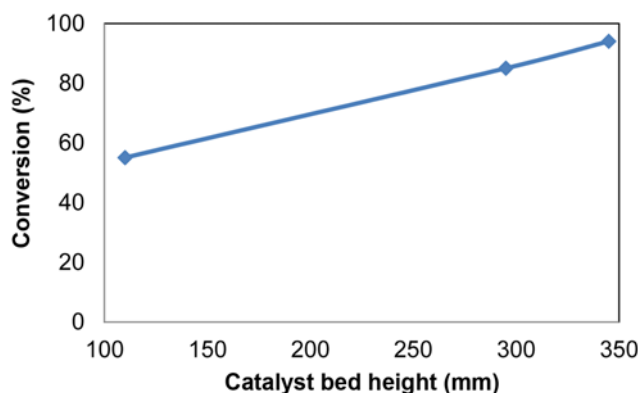Fig. 2. Effect of residence time on the conversion of transesterification in the fixed bed reactor.

Fig. 4. Effect of temperature on the conversion of transesterification in the fixed bed reactor.

Fig. 5. Effect of catalyst bed height on the conversion of transesterification in the fixed bed reactor.

Table 2. Reusability comparison between supported catalysts

Catalyst	Repeat run number	Remained catalytic activity	Reference
CaO/AC	4	70.1	This Work
KOH/AC	3	89.3	[27]
K_2CO_3/AC	3	97.4	[28]
CaO/Al_2O_3	2	95.8	[29]
KF/Al_2O_3	3	61.5	[30]
KNO_3/Al_2O_3	3	85.7	[31]
La_2O_3/ZrO_2	3	75.0	[32]

Fig. 4 shows that an increase in temperature led to higher reaction conversions, as expected. At the beginning of reaction, all yields were increased because reactant contacted fresh catalyst. Then the yields decreased due to slightly deactivated but stabilized catalyst [22,25], and the yields reached steady state in about 7-8 h reaction time. At 40 °C, the least yield (28.63%) was observed. At 50 °C, the yield was higher (49.32%). At 65 °C, the reaction conversion was highest (73.39%). Increasing the temperature to 70 °C, a fluctuation was observed with lower yield (not shown in Fig. 4). The temperature of 70 °C was higher than the boiling point of methanol (65 °C). Therefore, the vapor-liquid phases of the reaction mixture may be responsible for this fluctuation. Thus, the highest reaction temperature was limited to 60 °C for the transesterification of waste cooking palm oil in the fixed bed reactor.

The catalyst bed height in the fixed bed reactor is associated with the residence time during continuous transesterification. The influence of catalyst amount on the conversion is illustrated in Fig. 5. The conversion of WCO was greatly dependent on the catalyst applied. The conversion increased rapidly from 55.1% to 85.0% with the increase of the catalyst bed height from 110 mm to 295 mm. It demonstrates that a high catalyst bed height provides a longer reaction time and more active sites to promote the reaction between waste cooking palm oil and methanol at a given flow rate [18]. However, when the catalyst bed height exceeded 295 mm, the rate of reaction increased slightly. Therefore, the optimum catalyst bed height for biodiesel production in this research is found to be 295 mm.

The effect of initial water content in the feedstock on conversion by palm shell activated carbon supported calcium oxide solid-base catalyst in the fixed bed reactor was studied at the conditions of 1 ml/min feed flow rate, 25 : 1 methanol/oil molar ratio, 60 °C reaction temperature and 295 mm catalyst bed height. FFA conversion almost linearly decreased from 94.04% to 60.03% with an increase in water content from 0.1 to 4.8 wt%. It indicates that the presence of water hindered the ester formation with the transesterification, because the water molecules were absorbed on the active sites of the catalyst surface to form a water layer to block the accessibility of reactants to active sites [18,26]. As a consequence, it is necessary to relieve the initial water content in the feedstock in order to obtain a high FFA conversion.

2. Catalyst Reusability

Reusability of the CaO/AC catalyst in the transesterification of waste cooking palm oil under the optimum condition in the fixed bed reactor was studied. After each run, the used catalyst was taken out from the reactor and dried for reutilization. The catalytic activity remained 70.1% of the fresh catalyst when the activated carbon supported catalyst was employed for the fourth time. It was calculated based on the conversion of oil to methyl ester under the optimum condition. The decay in catalyst activity could be due to the leaching of active sites to the reaction media. Notwithstanding the interaction between the calcium species and activated carbon surface, the supported species are leached by the reaction media. Leaching of the active phase to the alcoholic phase can be attributed to the bond breaking and formation of Ca^{2+} and CH_3O^- [27]. As shown in Table 2, this value is within the range reported by other researchers [27-32].

3. Biodiesel Characterization

The waste cooking palm oil methyl ester produced under the optimum condition via transesterification in the fixed bed reactor was characterized for its physical and chemical properties. The results of these characterizations are listed in Table 3. As can be seen, the produced methyl ester using fixed bed reactor meets ASTM standard limits [33,34].

CONCLUSIONS

Aided by heterogeneous transesterification in the fixed bed reactor, high quality methyl ester was produced without needing washing and purification steps. The effects of parameters including methanol/oil molar ratio, feed flow rate, catalyst bed height and reaction

Table 3. Properties of final products derived from waste cooking palm oil

Properties	Waste cooking palm oil	Limits (ASTM)
Kinematic viscosity (mm^2/s, 40 °C)	5.8	1.9-6.0
Density (g/ml, 15 °C)	0.890	0.875-0.900
Flash point (°C)	180	≥130
Cloud point (°C)	12	-
Pour point (°C)	6	-
Acid value (mg KOH/g oil)	0.80	≤0.8
Iodine value (-)	58	-
Methyl esters content (%)	82.7	-
Water content (%)	0.03	≤0.05

temperature were found significant. The highest conversion of 94% was obtained at 60 ℃ reaction temperature, 8 h residence time, 295 mm packed bed height and 25 : 1 methanol/oil molar ratio. The mass transfer was observed to control the transesterification of waste cooking palm oil in a continuous fixed bed reactor. The conventional methods of increasing the mass transfer rates such as enhancement of active area per unit volume of catalyst could be useful in further studies. The characteristics of the product under the optimum condition were within the ASTM standard.

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