Production of Biodiesel from Waste Cooking Oil Using Transesterification, with the KOH on Carbon Support from Waste Material and Egg Shell, as the Catalyst

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Abstract

Microwave assisted transesterification of waste cooking oil (WCO) is carried out in the presence of KOH on carbonized waste coconut shell support (KOH/CS), and CaO derived from waste egg shell (CaO-ES). The effect of reaction temperature on the yield of Fatty Acid Methyl Esters (FAMEs) is studied. Conventional transesterification is also performed for comparison. FAME production is also carried out with new cooking oil (NCO). The results show that a reaction temperature of 80 °C is optimum for FAME production in the presence of either KOH/CS or CaO-ES. The produced biodiesel properties satisfy the criteria according to ASTM D6751**.** Acid catalysed esterification of WCO before transesterification leads to higher production of FAMEs due to the reduction of Free Fatty Acids (FFAs). However, conventional transesterification using WCO without esterification yields lower FAMEs. Although the microwave heating decreases the reaction time, it does not necessarily lead to an increase in FAMEs. The production of FAMEs depends on not only the type of transesterification process, but also the type of feedstock. Comparing KOH/CS with CaO-ES, KOH/CS is preferable in terms of the quantity and quality of the produced FAMEs using a two-step process with H_2SO_4 catalysed esterification, followed by alkali catalysed conventional transesterification.

Keywords: Biodiesel, Transesterification, FAME, FFA, Waste cooking oil

Received: 9 September 2016 Accepted: 18 November 2016
DOI:

1. Introduction

For over decades, many different ways have been developed to gain as much energy without using limited resources. Every year, millions of dollars have been spent on green energy research to find a new resource of energy. Biodiesel is one of the resources which will eventually take the place of petrol diesel. Among feedstocks for biodiesel production, palm oil has been widely used in Thailand and has the highest yield of biofuel oil plants (Pongpinyopap et al., 2014).

Biodiesel is an animal or vegetable oil based diesel fuel (Oliveira and Da Silva, 2013). The animal or vegetable oil is converted into biodiesel when a mole of triglyceride reacts with three moles of alcohol to produce a mole of glycerol and three moles of mono-alkyl esters. Since biodiesel is produced from animal and vegetable oils, which are renewable biomass sources, it has lower emissions of pollutants. The major drawback of biodiesel production is the cost of production. Since new vegetable oils and expensive catalysts are typically used, the cost of production increases tremendously. In this context, the use of waste cooking oil (WCO) instead of virgin oil to produce biodiesel is an effective way to reduce the raw material cost and the problem associated with the handling of WCO. Use of the catalysts derived from waste materials, opens the door for a renewable catalyst.

However, it has been reported that WCO contains a large amount of free fatty acids (FFAs) along with moisture, which should be removed to prevent soap formation (Canakci and Van Gerpen, 2001). Soap formation results in a low yield of biodiesel. When dealing with feedstocks containing high FFAs like WCO, alkali catalysts cannot directly catalyse the transesterification (Atadashi et al., 2012). To deal with this drawback, a two-step transesterification is recommended for high FFA oils (Canakci and Van Gerpen, 2001). In this technique, the first step is an acid catalysed process, which involves esterification of the FFAs to FAMEs, followed by a second step, alkali catalysed transesterification. For the first step, H_2SO_4 is the most common acid catalyst used due to its good catalytic activity and the simplicity of H_2SO_4/methanol preparation. Concentrated H_2SO_4 can be added directly to methanol. For the second step, there are several heating systems employed. The conventional transesterification process is an open system, performed in a glass reactor with a condenser to reduce the loss of methanol. An alternative heating system, that is, microwave irradiation, was reported to be superior to conventional system (Hsiao et al., 2011). By using microwave irradiation, the reaction time can be shorter. Moreover, there are two types of alkali catalysts which can be employed for alkali catalysed transesterification, namely, homogeneous alkali catalyst and heterogeneous alkali catalyst. The latter is preferred due to easy separation and reusability. The overall production cost can be lower with a heterogeneous system since it simplifies the production and purification processes and eliminates the need for the neutralization of catalyst with acid (Fukuda et al., 2001). The higher selectivity of heterogeneous

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ISSN 1686-5456(Print)
ISSN 2408-2384(Online)

alkali catalyst can also prevent undesirable side reactions, leading to reduced environmental impact (Fukuda et al., 2001). Apart from these advantages, the activity of a heterogeneous alkali catalyst was also found to resemble a homogeneous counterpart at the same operating conditions (Kim et al., 2004).

Based on those rationales, this research was carried out to obtain biodiesel from WCO through transesterification with microwave heating. Conventional transesterification was used for comparison. A two-step process involving esterification of WCO, with H_2SO_4 in the first step, was also applied. The effect of reaction temperature during microwave heating on the FAME production was investigated. KOH supported on carbonized coconut shell carbon (KOH/CS), and CaO derived from egg shell, both support and catalyst produced from waste material, were employed as heterogeneous alkaline catalysts. The novelty of this study is that, both catalyst material and biodiesel feedstock, are waste materials. Utilization of these waste materials as both feedstock and catalyst promotes an environmentally benign process for biodiesel production. The newly developed KOH/CS and CaO were evaluated for biodiesel production using WCO as feedstock.

2. Methodology

2.1 Materials

New oil and waste cooking oil used in the study were collected from Useful Food Co., Ltd., Bangkok, Thailand. Density, viscosity, FFA and Fatty Acid Methyl Esters (FAMEs) of NCO and WCO were determined according to standard methods from GC analysis of total Fatty Acid Methyl Esters (FAMEs), and methyl linolenate in biodiesel was done using the revised EN14103:2011 method (Agilent Technologies, 2012).

2.2 Catalyst preparation

The heterogeneous alkali catalysts selected in the study are KOH supported on the carbonized coconut shell and CaO derived from egg shell. For carbonization of coconut shell (CS), the coconut shell was first cleaned with water and dried at room temperature for 24 hrs. It was then crushed with a blender, sieved to 600-1000 μm, and carbonized in a furnace at 700 °C for 2 hrs. The obtained black charcoal was furthermore subjected to impregnation with KOH. For impregnation with KOH, 10 g of the obtained CS was cleaned with deionized water, and filtered and dried in an oven at 105 °C for 12 hrs. Subsequently, 37.5 g of KOH was dissolved in 150 ml of deionized water and the CS was added into this KOH solution at room temperature under agitation in a shaker at 180 rpm for 24 hrs. The obtained product was filtered, dried in an oven at 150 °C for 24 hrs, and kept in a close vessel to avoid the reaction with humidity. The amount of KOH impregnated in CS was determined by the back titration method (Babić et al., 1999) and found to be 31.2 g in 10 g of CS.

For preparing CaO from egg shell, a calcination-hydration-dehydration process was employed. First, the egg shell was washed with tap water to remove unwanted material on its surface, followed by rinsing with distilled water. It was then dried in a hot oven at 105 °C for 24 hrs, ground into small pieces, calcined in a muffle furnace at 900 °C for 2.5 hrs, and refluxed with deionized water at 60 °C for 6 hrs. The CaO obtained was filtered, dried in hot air oven at 105 °C overnight and finally dehydrated through calcination at 600 °C for 3 hrs. The solid product was kept in the closed vessel to avoid reaction with CO_2 and humidity.

2.3 Pretreatment of oil for esterification of FFA

For acid catalysed esterification, 120 g of oil was first poured into 250 ml three-neck round-bottom flask and heated to reach the desired temperature of 65 °C. Then, 27.2 g of methanol and 0.6 g of H_2SO_4 were poured and mixed in the flask under continuous stirring. The reaction was kept at 65 °C for 2 hrs and allowed to cool down to room temperature. The mixture was poured into a separatory funnel. The ester layer, located in the upper layer, was separated by gravity. The glycerol, extra methanol, and undesired products were in the lower layer, and were decanted. The ester layer was washed several times with a small amount of hot water until the washings were neutral. The ester layer was then dried over sodium sulphate, filtered, and kept in the refrigerator for transesterification.

2.4 Microwave assisted transesterification

The microwave assisted transesterification was performed in a microwave (MARS 6, 240/50). First, 10 g of oil, 0.5 g of catalysts, and 4.35 g of methanol were poured into vessel and put in a microwave for 40 mins with a ramping time of 10 mins. A methanol to oil ratio of 12:1 was employed (Niju et al., 2014). The operating temperature was varied (60, 70, 80, and 90 °C). After 40 mins, the mixture was filtered and poured into a separating funnel. The ester layer was separated by gravity, and located in the upper layer. The glycerol, extra methanol, and undesired products were in the lower layer and were decanted. The ester layer was washed several times with a small amount of hot water until the washings were neutral. The ester layer was then dried over sodium sulphate, filtered, and kept in the refrigerator, to reduce the chance of oil decomposition for further analysis of ester amount by Gas Chromatography (HP-INNOWax Column). The analysis was based on EN14103 with methyl heptadecanoate (C_{17}) as the internal standard and heptane (C_7H_{16}) as the solvent. The %FAME was calculated from:

$$\%FAME = \frac{\sum A - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100 \qquad (1)$$

Where;

$\sum A$ = total peak area of FAME (C14 – C24)
A_{EI} = peak area of standard (C17)
C_{EI} = concentration of standard (C17, mg/mL)
V_{EI} = volume of standard solution (mL)
m = mass of product (mg)

2.5 Conventional transesterification

The transesterification was carried out in a 250 ml three-neck round-bottom flask. The reactor was placed in a heated oil bath. Catalyst (1.5 g) was put into the flask containing 30 g of oil. The flask was heated to 65 °C under continuous stirring and 13.1 g of methanol was then poured into the flask. The methanol to oil ratio was kept at 12:1 during the study. The reaction was kept at a desired temperature for 2 hrs and allowed to cool down to room temperature. The mixture was filtered and subjected to a separation process, which was the same as that for microwave assisted transesterification.

3. Results and Discussion

3.1 Oil properties

Table 1 summarizes the properties of NCO and WCO. As can be seen, the density of NCO and WCO is similar. However, WCO has slightly higher density due to the small particles from food processing and some food contaminants. Figure 1 shows the appearance of NCO and WCO. The colour of WCO is darker than that of NCO. Comparing the viscosity of NCO and WCO, WCO has a higher value. The higher viscosity of WCO is due to the presence of food contaminants and due to reactions occurring during food processing such as oxidation and polymerization, which can increase the viscosity of the oil. Although WCO has higher FAMEs, its FFA is also higher than that of NCO. Thus, the amount of FFA needs to be reduced through esterification with homogeneous acid catalyst, which was done in this study.

Table1: Properties of NCO and WCO

Property	NCO	WCO
Density (g/cm^3)	0.9017	0.9057
Viscosity (mm^2/s)	75.5575	78.6338
Acid number (mg KOH/g oil)	0.5589	1.3602
FFA (%)	0.2794	0.6801
FAME (%)	1.0135	1.3053

Figure 1: Appearance of NCO (A) and WCO (B)

3.2 SEM analysis and BET analysis for catalyst characterization

Figure 2 shows the SEM images of KOH/CS and CaO-ES. As seen, the surface of CaO-ES has larger pore size. Therefore, it is easier for the reactants to enter the pores. Also, the surface of CaO-ES is rougher, which is beneficial to accommodate more reactants. For BET analysis, the result shows that KOH/CS has a BET surface area of 0.8 m^2/g and mean pore size of

15.7 nm, and CaO-ES has a BET surface area of 11 m^2/g and mean pore size of 25 nm. Based on all these results, CaO-ES is expected to show better performances.

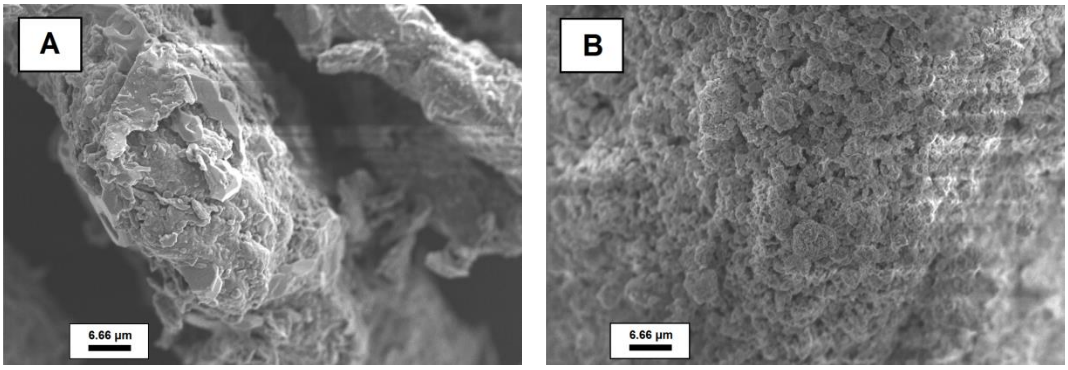

Figure 2: SEM image of KOH/CS (A) and CaO-ES (B)

3.3 Esterification of WCO

Table 2 shows the properties of WCO after being esterified with H_2SO_4. As shown, after esterification, density, viscosity, and FFAs decrease while FAMEs increases. These changes are beneficial for subsequent transesterification process. In particular, the FFA content in treated waste cooking oil (TWCO) is smaller than those in NCO and WCO. This indicates that FFAs can be changed into methyl ester through the esterification with H_2SO_4. Based on this finding, acid catalysed esterification is proven to be suitable for stockfeeds with high FFAs like WCO, which are low grade oil.

Table 2: Properties of TWCO

Property	TWCO
Density (g/cm^3)	0.9034
Viscosity (mm^2/s)	70.2314
Acid number (mg KOH/g oil)	0.8058
FFA (%)	0.4029
FAME (%)	4.6755

3.4 Transesterification

In this research, two transesterification processes, microwave assisted transesterification and conventional transesterification, were performed and compared. NCO, WCO, and TWCO were used as feedstocks for transesterification. For transesterification with microwave heating, the reaction temperature was varied. In fact, transesterification can occur at different temperatures, depending on the properties of oils. This can be at ambient temperature or at a temperature close to the boiling temperature of methanol. However, high reaction temperatures typically speed up the reaction and shorten the reaction time.

3.4.1 Transesterification with KOH/CS

Figure 3 shows the effect of temperature on the FAME production from NCO at a methanol to oil ratio of 12:1 in the presence of KOH/CS with a microwave assisted process. With increasing the temperatures from 60 °C to 80 °C, the FAME production increases more than 44 %. However, when the temperature increases to 90 °C, there is a reduction of the FAME production. This may be due to four factors. First, high temperature enhances not only transesterification but also saponification, which is detrimental to FAME formation. Second, at the beginning of the reaction, the FAME production increases because reactant contacts fresh catalyst. Then, it decreases due to a slight deactivation of the catalyst. Third, 90 °C is quite far from the boiling point of methanol (65 °C). Hence, chances of methanol loss are high. Fourth, at high temperatures, a large number of bubbles easily occur and can inhibit the reaction in the three-phase interface (oil–methanol-catalyst).

Moreover, the trend of FAME production using WCO is also the same as that using NCO (Figure 3). At 60 °C, the least conversion (23.21%) is observed. At 80 °C, the reaction conversion is highest (80.89%). With increasing the temperature to 90 °C, a decrease of FAME production is observed. In all the cases for three different oils, the optimum reaction temperature is found to be 80 °C.

Comparing the oil used in the microwave assisted transesterification with KOH/CS, the use of TWCO enables higher yields of FAMEs in all the temperatures applied (Figure 3). This indicates that the two-step process involving acid catalysed esterification in the first step can be a better option for producing biodiesel from feedstocks with high FFAs like WCO. The FFAs in the feedstock can be decreased, first through esterification, before the feedstock is subjected to alkali catalysed transesterification.

For comparison, conventional transesterification was also performed. The results show that NCO is a better feedstock compared to WCO since it leads to higher yields of FAMEs (Figure 4). This is obviously because NCO contains lower FFAs (Table 1). Moreover, TWCO is found to be the best feedstock due to the same reason. It contains the lowest FFAs, allowing effective production of FAMEs. These results are similar to those of microwave assisted transesterification. Reduction of FFAs through acid catalysed esterification is proven to result in a higher yield of FAMEs. Furthermore, using TWCO as feedstock, conventional transesterification yields slightly higher FAMEs but with a longer reaction time. Long reaction time is actually the main drawback in a conventional process as compared to a microwave assisted one. Similar results on the production of biodiesel using microwave heating were also reported. It was found that the application of radio frequency microwave energy enhanced the rate of biodiesel production from Jatropha oil (2 mins instead of 150 mins) and improved the separation process (El-Sherbiny, et al., 2010). A remarkable enhancement of esterification with microwave heating for biodiesel production using cation ion exchange resin particles (CERP) coated on ployethersulfone (PES) catalytic membrane was also reported by Zhang et al. (2012). The FFAs conversion, of microwave assisted esterification, reached 97.4% at a temperature of 60 °C, methanol/acidified oil mass ratio of 2:1, catalytic membrane loading of 3 g, microwave power of 360 W, and reaction time of 90 mins.

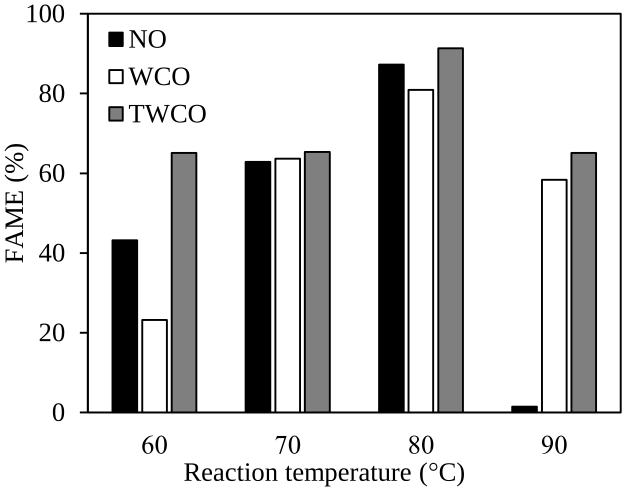

Figure 3: Effect of reaction temperature on the FAME production with microwave assisted transesterification of NCO, WCO, and TWCO in the presence of KOH/CS with operating temperature at 60, 70, 80, and 90 °C, reaction time 40 minutes, methanol-to-oil ratio 12:1, and 5 wt% ratio of catalyst-to-oil

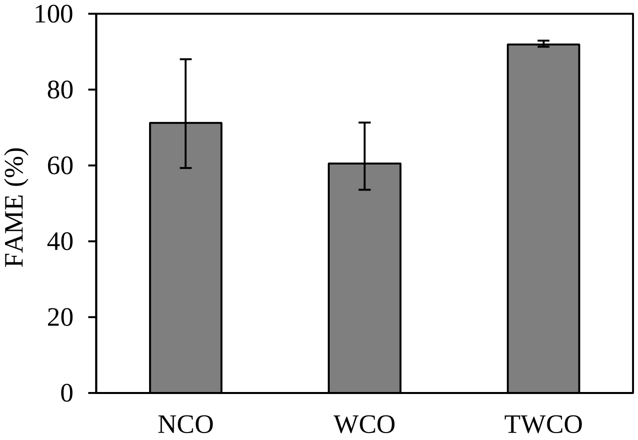

Figure 4: FAME production with conventional transesterification in the presence of KOH/CS with operating temperature at 65 °C, reaction time 90 minutes, methanol-to-oil ratio 12:1, and 5 wt% ratio of catalyst-to-oil

3.4.2 Transesterification with CaO derived from egg-shell

As can be seen in Figure 5 for the microwave assisted transesterification, increasing temperature increases the FAME production. Such a positive effect of temperature on the FAME production is also observed in the FAME production using KOH/CS. The reaction temperature plays a significant role in increasing the production of FAMEs up to a certain extent. In the presence of CaO, the FAME production increases drastically with increasing temperature from 60 to 70 °C. The increase of FAME production becomes insignificant with increasing temperature from 70 to 80 °C, especially transesterification using WCO and TWCO. Transesterification at elevated temperatures appears to be detrimental to FAME production. Furthermore, using NCO as feedstock, the FAME production at 80 °C is very high, up to 97%. An appreciable FAME production (83.8%) can still be achieved under the same experimental conditions using WCO as a feedstock.

The FAME production can be slightly enhanced by applying esterification to WCO as can be seen in Figure 5. In all the temperatures applied, the FAME production increases. These FAME production increases are attributed to the reduction of FFA content after esterification. However, the increase of FAME production becomes insignificant with increasing temperature. At 80 °C, the increase of FAME production is only 3.18%. This result, again, proves that elevated temperature can be unfavourable to the transesterification efficiency.

The pattern of the FAME production with conventional transesterification is also similar with those with microwave heating. Use of NCO as a feedstock results in the highest FAME production, and esterification before transesterification (TWCO) leads to increased FAME production (Figure 6). Interestingly, the positive effect of esterification on the FAME production is more pronounced in the case of conventional transesterification. Esterification significantly enhances the FAME production from 24.3% (using WCO) to 77.1% (using TWCO). Hypothetically, CaO should be better than KOH/CS for the FAME production, which is due to several factors. First, CaO is highly basic (Zu et al., 2010). According to a pH test by universal indicator, its pH is close to 14. It is known that effective transesterification for FAME production highly depends on the amount of basic sites. Second, alkali earth metal compounds like CaO feature lower solubility in methanol, and they are not corrosive in nature (Kesić et al., 2016). Third, as seen in this research, CaO possesses a higher specific surface area, providing better access for the conversion of reactants into products. However, based on all the results obtained for the FAME production, the performance of CaO with conventional heating is generally inferior to that of KOH/CS although it leads to higher efficiency using microwave heating. The reason for a high yield of biodiesel with conventional heating by using KOH/CS is likely due to the fact that the carbon support provides well-distributed KOH on the surface with no interference effect from the support (Saeid Baroutian, 2010). The pathway for the transesterification catalyzed by KOH/CS should follow a similar mechanism to that of a homogeneous base catalyst (Koh et al., 2011), namely: (i) absorption of methanol on the catalyst surface, producing catalytic active species (CH_3O-), (ii) nucleophilic attack of CH_3O- on the carbonyl carbon of triglyceride, forming a tetrahedral intermediate, (iii) rearrangement of the intermediate, resulting in the formation of FAME and finally (iv) conversion of protons to diglyceride ion, generating diglyceride. This pathway was then repeated twice to yield glycerol and biodiesel. Overall, it seems that CaO derived from egg shell is preferable to KOH/CS due to the above mentioned factors as well as its lower price.

Several new heterogeneous catalysts, such as catalytic membranes, have also been developed to overcome the shortcomings of a liquid acid catalyst. Catalytic membranes have especially attracted significant attention due to their easy removal from the reaction mixture, allowing mild reaction conditions without corrosion to equipment and pollution to the environment. It was reported that hybrid catalytic membranes, consisting of cation ion-exchange resin particles (CERP) and polyethersulfone (PES), are very effective as heterogeneous catalysts for the esterification of acidified oil with methanol, ethanol, propanol, and butanol. The highest FFAs conversion of 95.28% can be obtained with butanol (Zhang et al., 2012). Sulfonated cation exchange resins (s-CERs) incorporated in a polyvinyl alcohol (PVA) matrix is also used as a replacement of liquid acids for the catalytic esterification of FFAs to produce biodiesel (Zhang et al., 2016). Employing s-CER/PVA, FFA conversion was increased from 80.1% to 97.5% after 8 hours, and the turnover frequency (TOF) was increased more than 3.3 times. The TOF of s-CER/PVA was also 2.6 times higher than that of sulphuric acid.

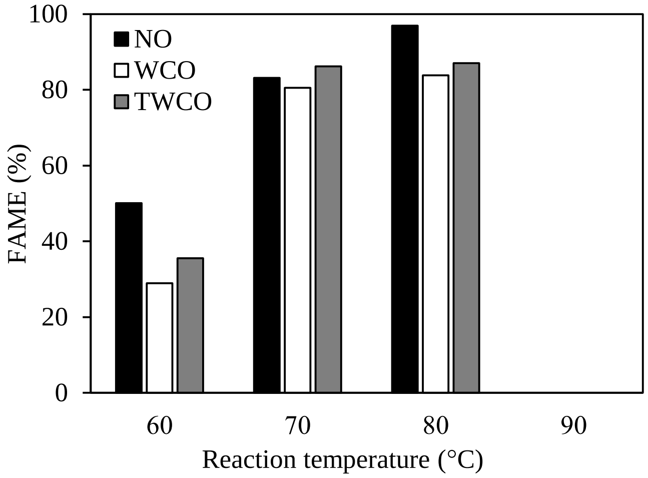

Figure 5: Effect of reaction temperature on the FAME production with microwave assisted transesterification of NCO, WCO, and TWCO in the presence of CaO derived from egg-shell with operating temperature at 60, 70, 80, and 90 °C, reaction time 40 minutes, methanol-to-oil ratio 12:1, and 5 wt% ratio of catalyst-to-oil

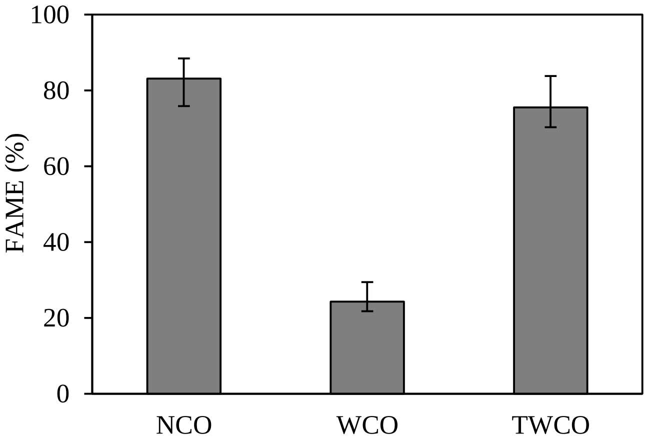

Figure 6: FAME production with conventional transesterification in the presence of CaO derived from egg-shell with operating temperature at 65°C, reaction time 90 minutes, methanol-to-oil ratio 12:1, and 5 wt% ratio of catalyst-to-oil

3.5 Biodiesel properties

The properties of biodiesel obtained from the two-step process with H_2SO_4 catalysed esterification in the first step and KOH/CS catalysed conventional transesterification in the second step are summarized in Table 3. It can be seen that most of the properties meet the standard criteria of biodiesel according to ASTM D6751. The density of the biodiesel obtained is less than those of NCO, WCO, and TWCO because of the change in chemical structure from triglyceride to methyl ester. The molecules pack tightly and require less volume. The density of biodiesel is also within the standard. Furthermore, comparing the viscosity of produced biodiesel with those of the raw material, the viscosity of the biodiesel is much lower. This low viscosity is a good property for fuel. The viscosity is very close to the standard. In fact, to decrease the viscosity of the produced biodiesel, one can add low density diethyl ether (DEE) to the biodiesel (Kannan et al., 2010). Addition of DEE to biodiesel can also reduce smoke opacity and NO_x emission. Regarding the acid number, it is in the range of the standard. Actually, if it is required, the acid number can still be decreased by a neutralization reaction or washing the biodiesel.

Replacing KOH/CS with CaO leads to slightly lower properties of biodiesel. KOH/CS seems to be preferable to CaO in terms of quantity and quality of the FAME production, using the two-step process with H_2SO_4 catalysed esterification in the first step, and alkali catalysed conventional transesterification in the second step.

Table 3: Comparison of produced biodiesel with ASTM D6751 standard

Property	Biodiesel from this work		ASTM D6751
	KOH/CS	CaO	
Density, @ 15.5 °C (g/cm^3)	0.8596	0.8591	0.8747
Kinematic Viscosity, 40 °C (mm^2/s)	6.6009	6.6047	1.9–6.0
Acid Number (mg KOH/g oil)	0.2171	0.2987	0.50 max.

4. Conclusion

Transesterification of WCO in the presence of KOH/CS and CaO is successfully carried out through microwave and conventional heating. The properties of the obtained biodiesel obtained are very close to the standard, according to ASTM D6751. Furthermore, the following conclusions can be made:

- Reaction temperature plays a critical role in the FAME production under microwave heating in the presence of KOH/CS and CaO. Increasing temperature increases the FAME production up to an optimum value. A reaction temperature of 80 °C leads to the highest production of FAME.
- The highest FAME production of 91.3% under microwave heating is obtained using 5 wt.% KOH/CS, alcohol to oil ratio of 12:1, 80 °C, and 40 min reaction time. In the presence of CaO under identical experimental conditions, the highest FAME production reaches 87%. On the basis of these results, microwave heating is shown to be a promising technique for biodiesel production in a short reaction time with appreciable FAME yields.
- The performance of conventional transesterification is comparable to that of microwave assisted transesterification. However, pretreatment with acid catalysed esterification must be done before the transesterification process to reduce the FFA content in the feedstock. Such pretreatment is appropriate for feedstocks with a high content of FFAs.
- KOH/CS is a better alkali catalyst for transesterification using conventional heating while CaO is preferred for transesterification using microwave heating.

5. Acknowledgement

The authors would like to acknowledge the facilities provided by the Sirindhorn International Institute of Technology, Thammasat University.

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