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# Biodiesel production from waste cooking oil using a new heterogeneous catalyst SrO doped CaO nanoparticles

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**Abstract**

Biodiesel production from waste palm cooking oil (WPCO) was studied. Calcium oxide with a strontium ion additive (Sr-CaO) was employed as a catalyst in transesterification reaction of used palm oil with methanol. The Sr-CaO was synthesized by co-precipitation method between $SrCl_2$ and $Ca(NO_3)_2$, then calcined at 900°C for 5 h. The catalyst was characterized by using thermo-gravimetric analysis (TGA), X-ray diffraction (XRD), Scanning electron microscope (SEM), and Fourier transform infrared spectrometer (FT-IR). The morphology and elements content of Sr and Ca in the catalyst were confirmed by SEM-EDX. The approximate catalyst diameter is 12.6±5.9 µm. The highest conversion was 99.33% (the reaction time 3 h, 5%w/w catalyst, methanol to oil molar ratio 9:1 and reaction temperature 80°C). The catalyst can be used up to the sixth cycles with a good yield. The synthesized biodiesel meet the requirement of standard biodiesel (EN 14103 and ASTM D445). These findings suggest that calcium oxide with a strontium ion additive (Sr-CaO) is an effective renewable biodiesel catalyst.

## 1. Introduction

During the past two decades, the world energy demand has increased every year, mainly due to population growth; the increased industrial, economic, and society development, and associated transportation. Most of this energy is supplied from the combustion of non-renewable fossil fuels, such as petroleum oil, natural gas, and coal [1]. However, these supplies are continuously decreasing, whilst their combustion leads to environmental problems, such as the release of greenhouse and toxic gases. Thus, there is a growing need and demand to find other alternative and sustainable energy sources. Biodiesel, is one of the more interesting alternative energy sources because it is renewable, biodegradable, emits a low-level of greenhouse gases, and is environmental friendly [2-4]. Biodiesel can be produced from the transesterification of a fat or oil with an alcohol, such as methanol or ethanol to yield fatty acid methyl esters (FAME) or fatty acid ethyl esters, respectively, as the main product (biodiesel) with lower levels of glycerol (10% by weight) and minor contaminants, such as fatty acids [5-7]. The transesterification catalyst for biodiesel production can be either homogeneous or heterogeneous [8]. At an industrial scale, homogeneous alkaline base catalysts, such as sodium hydroxide or potassium hydroxide, are usually used because they result in a very high biodiesel conversion level and require only a mild reaction condition [9-12]. However, these catalysts can cause many problems, such as it is difficult to separate the catalyst from the biodiesel product, it produces a large amount (10% by volume of the biodiesel) of toxic wastewater from the catalyst separation process that requires treatment before discharge to the environment, is sensitive to free fatty acid levels in the feedstock, and the catalyst can't be reused. To solve those problems, heterogeneous catalysts have been evaluated for biodiesel production because they are reusable, easy to separate after the reaction is complete, and are more environmentally friendly than homogeneous catalysts [2,13]. However, heterogeneous catalysts still have some disadvantages, such as a loss of surface area after each reaction and the requirement for a longer reaction time to complete the reaction. Therefore, to solve these problems, attempts to improve their catalytic activity are important. The popular technique to improve catalysts is to dope them with a suitable metal ion, since this can increase the efficiency and activity of the catalyst, increase the surface area of the catalyst, maintain a high catalytic activity after multiple runs, reduce the leaching problem, and decrease the reaction time [14-18].

Among alkaline-earth metal oxides, strontium oxide (SrO) has also attracted attention as a heterogeneous catalyst owing to its high basicity and its insolubility in methanol, vegetable oil, and FAMEs. Biodiesel production from soybean oil using a SrO catalyst gave a 95% FAME yield, had a long catalyst life time, and could be reused for 10 cycles [19]. The biodiesel production from olive oil using a SrO/calcium oxide (CaO) and a SrO/silica ($SiO_2$) catalyst resulted in biodiesel production at up to 82% in only 10 min, and the catalyst

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could be reused for five cycles with a biodiesel yield higher than 60% [17]. The transesterification reaction with CaO, and SrO doped with $K_3PO_4$ exhibited a strong catalytic activity to give a biodiesel yield in the range of 78% to 92% [20].

For catalyst formation, the co-precipitation method has been found to be one of the interesting methods for modification of CaO and SrO catalysts because this method can produce the modified catalyst with a high basicity, large surface area, and high catalytic activity [21-24].

In this work, strontium-doped CaO (St-CaO) was synthesized and evaluated as a potential catalyst for FAME production via the transesterification of waste palm cooking oil (WPCO) with methanol. The physical and chemical characterizations of the obtained calcined catalysts were investigated. The effects of the transesterification reaction, including the methanol:oil molar ratio, catalyst loading level, reaction time, and reusability of the catalyst, were evaluated, and reported.

## 2. Experimental

### 2.1 Materials

Strontium chloride hexahydrate ($SrCl_2{\cdot}6H_2O$, AR Grade), and calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$, AR Grade) and sodium carbonate anhydrous ($Na_2CO_3$, AR Grade) were purchased from Ajax Finechem, Australia). Used palm oil were obtained from Patumthani province, Thailand with acid value 1.2 mg KOH per gram.

### 2.2 Catalyst preparation

#### 2.2.1 Synthesis of calcium oxide with strontium ion additive

The Sr-CaO catalysts were prepared by the co-precipitation of $Ca(NO_3)_2{\cdot}4H_2O$ and $SrCl_2{\cdot}6H_2O$ at different weight ratios (wt%) of $Ca(NO_3)_2{\cdot}4H_2O$ to $SrCl_2{\cdot}6H_2O$ solutions of 50, 10, 7, 5, 3, and 1 wt%. Excess 1 M $Na_2CO_3$ solution (50 mL) was slowly added with continuous stirring for 3 h at room temperature to ensure the reaction was complete. The synthesized catalyst was then harvested by filtration, dried for 10 h at 100°C in an oven, and calcined at 900°C for 5 h. The solid catalyst obtained after calcination was ground and kept in a desiccator for further use.

#### 2.2.2 Catalyst characterization

The physical and chemical properties of the catalysts were characterized using Fourier-transform infrared spectroscopy (FTIR) over 4000 $cm^{-1}$ to 400 $cm^{-1}$, thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) and nitrogen adsorption-desorption with Brunauer-Emmett-Teller (BET) analyses. The biodiesel conversion level was analyzed from the proton nuclear magnetic resonance ($^1H$-NMR) spectra were recorded at 400 MHz. The basic strength of the catalysts was analyzed qualitatively using the Hammett indicators methyl red, bromothymol blue, phenolphthalein, 2,4-dinitroaniline, and 4-nitroaniline.

### 2.3 Synthesis of biodiesel by transesterification of WPCO with methanol

The transesterification of WPCO and methanol was performed by refluxing at 80°C using different methanol: oil molar ratios (1:1, 3:1, 5:1, and 9:1), catalyst concentrations (5, 10, 15, and 20 wt%), and reaction times (3, 4, 5, and 7 h) in a univariate analysis approach. The catalyst was removed from the biodiesel by filtration, and the WPCO conversion to FAMEs was determined in terms of the %FAME; calculated from the 2:3 ratio of integration of the $^1H$-NMR signals between the methoxy protons ($CH_3O$-) of the methyl esters ($ACH_3$) at a chemical shift of 3.68 ppm and the ethylene protons ($CH_3$-) of triglyceride ($ACH_2$) at a chemical shift of 2.30 ppm [25], as shown in Equation (1), calculation of biodiesel conversion [26]

$$\%\,FAME = \frac{2 \times A_{CH_3}}{3 \times A_{CH_2}} \times 100\% \tag{1}$$

### 2.4 Catalyst reusability

After each reaction, the catalyst was retrieved by filtering, washing with hexane several times to remove the unreacted oil, drying at 120°C, and then used in the next cycle.

### 2.5 Biodiesel properties test

#### 2.5.1 Density test

Each biodiesel sample (5 mL) was extracted using a syringe and weighed three times, recording the average weight. The density was calculated from D = M/V, where D is the density ($g{\cdot}mL^{-1}$), M is the weight of oil (g), and V is the volume of oil (mL), in accord with ASTM D 1298.

#### 2.5.2 Cloud point and pour point test

The biodiesel product was poured into a test tube containing a thermometer and immersed in an ice bath. The cloud point was observed by the appearance of a white spot in the oil, and the temperature at which the cloud point appeared was recorded. The pour point was found by tilting the tube at 90° and recording the temperature at which the oil became solid. These were in accord with the ASTM D 2500 and ASTM D 97 standard methods.

#### 2.5.3 Flash point test

This was conducted using a Petrotest TV 40002 in accord with the ASTM D 93 standard. The oil was heated until a flash of ignition was observed, and the temperature was recorded.

#### 2.5.4 Viscosity test at 40℃

Biodiesel was poured into the bulb of the viscometer, heated to 40℃ and held at this temperature for 30 min. The time was recorded when the biodiesel started to flow into the bowl until it reached the end. The time the oil took to flow through the bulb was derived. The viscosity was calculated from the time taken for the oil to flow and the constant of the bulb, as per ASTM D 445.

# 3. Results and discussion

## 3.1 Catalyst characterization

### 3.1.1 Thermal stability

The decomposition patterns of both the non-calcined and calcined 3% Sr-CaO were studied by TGA (Figure 1). The calcined sample was kept in atmospheric storage for four weeks, prior to the analysis. The non-calcined 3% Sr-CaO (Figure 1(a)) showed two major decomposition steps of carbon dioxide ($CO_2$) removal at 650°C to 760°C and 800°C to 900°C. The previous reported the phase changes of $CaCO_3$ to CaO occur at 602°C to 811°C and of $SrCO_3$ to SrO at 813°C to 947°C [26]. Since the goal of the current research was to convert all the $CaCO_3$ and $SrCO_3$ to CaO and SrO, calcination at 900°C for 5 h was selected [27].

Since atmospheric moisture and $CO_2$ may affect the phase change of CaO, the calcined catalyst was stored under ambient conditions for four weeks before the TGA analysis. The TGA of the calcined 3% Sr-CaO catalyst is shown in Figure 1(b), where the first decomposition step at 350°C to 400°C (weight loss of 1.31%) was related to the removal of water from the $Ca(OH)_2$ to form CaO [28], and the second step at 650°C to 800°C was assigned to $CO_2$ removal from the $CaCO_3$. It can be concluded that the CaO absorbs water and trace $CO_2$ at room temperature to form $Ca(OH)_2$ and $CaCO_3$, respectively.

### 3.1.2 X-ray diffraction pattern

The calcined $SrCO_3$ catalyst showed an incomplete phase change, as shown in Figure 2(a). However, the presence of SrO was identified at a $2\theta$ value of 29°, 33°, and 50°. The XRD patterns of the CaO, 3% Sr-CaO, and 10% Sr-CaO exhibited peaks, corresponding to the face center cubic crystal structure of CaO at $2\theta$ values of 32.34°, 37.52°, 53.98°, 64.20°, and 67.42° with lower intensity peaks at $2\theta$ values of 19°, 25° and 33°, which corresponded to the presence of the hexagonal crystal structure Portlandite (calcium hydroxide; $Ca(OH)_2$) [29] formed from the spontaneous reaction between CaO and moisture in air. The XRD pattern of the 50% Sr-CaO catalyst showed strong intensity peaks of SrO and CaO with $SrCO_3$ impurity at a $2\theta$ of 32.24°, 37.42°, 53.88°, 63.58°, and 66.88°, corresponding to CaO and low intensity peaks at a $2\theta$ of 34.8° and 50° that corresponded to the cubic phase of SrO. The XRD pattern of SrO found in this work was similar to the pure SrO pattern reported previously with peaks at a $2\theta$ of 29°, 33°, and 50° [30]. Increasing the $Sr^{2+}$ loading from 3 wt% to 50 wt% altered the diffraction intensity to a new pattern where SrO become more dominant with intense peaks due to $SrCO_3$.

### 3.1.3 FTIR spectroscopy

The FTIR spectra of the 3% Sr-CaO catalyst after being calcined at 900°C for 5 h and kept in air for 4 weeks is shown in Figure 2(b), as a representative example of all the Sr-CaO catalysts. Asymmetric C=O stretching peaks of carbonate ($CO_3^{2-}$) were found at 1521 $cm^{-1}$ and from 2800 $cm^{-1}$ to 2900 $cm^{-1}$ [29]. The 3% Sr-CaO catalysts showed the C=O vibration peaks of the carbonate ($CO_3^{2-}$) group and symmetric stretching at 1790 $cm^{-1}$ and 2527 $cm^{-1}$, respectively, and a sharp peak for the -OH stretching of $Ca(OH)_2$ at 3630 $cm^{-1}$ and a small stretching vibration peak [31].

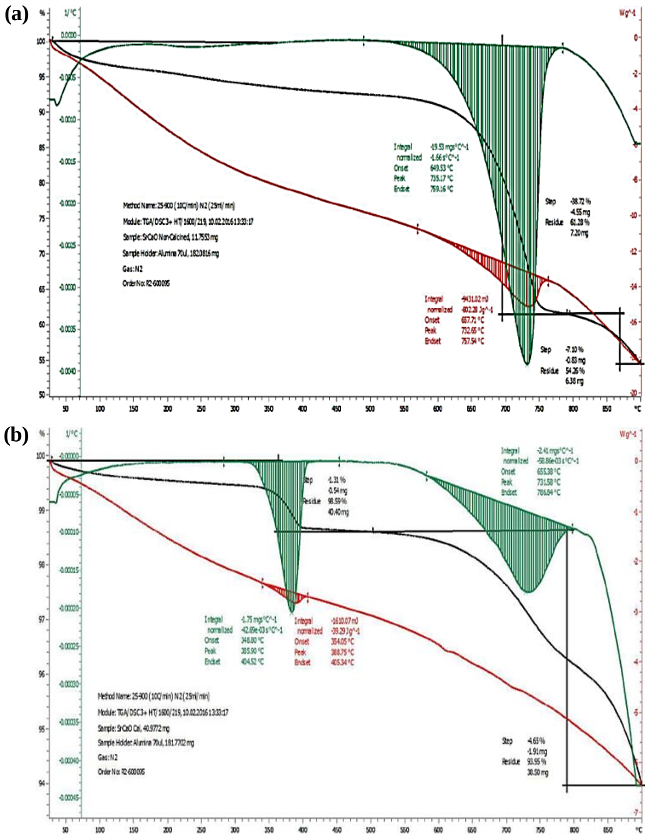

**Figure 1.** Representative TGA curve of the (a) non-calcined and (b) calcined (900°C for 5 h) 3% Sr-CaO catalyst stored in air for 4 weeks.

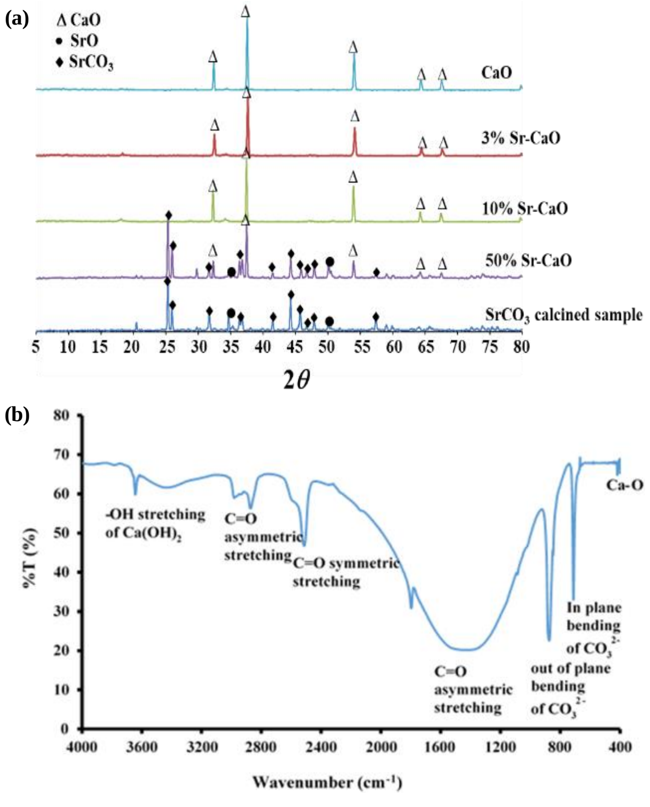

**Figure 2**. Representative (a) XRD patterns of the CaO, the 3%, 10%, and 50% Sr-CaO, and the $SrCO_3$ calcined catalyst, and (b) FTIR spectra of the 3% Sr-CaO.

### 3.1.4 Surface morphology

The surface morphology and particle size of the Sr-CaO and reused 3% Sr-CaO catalysts were studied by SEM, while the percentage of $Sr^{2+}$ ions in the Sr-CaO catalysts were studied by EDX. The SEM image of calcined Sr-CaO and reused 3% Sr-CaO catalyst showed a similar morphology in all the samples, with an example shown in Figure 3. When the concentration of $Sr^{2+}$ was increased up to 10%, a rougher surface with less pores on the catalyst surface was evident, which may have resulted from the coating of excess $Sr^{2+}$ ions on the CaO catalyst. Likewise, barium ion-doped CaO also showed similar evidence [32]. The primary particle size was gradually increased when the concentration of strontium ion was increased as shown in the Figure 3(e).

### 3.1.5 BET surface area

The $Sr^{2+}$ loading increased from 3% to 5%, 7%, and 10%, the $S_{BET}$ decreased from 55.98 to 12.03, 7.53, and 5.11 $m^2 \cdot g^{-1}$, respectively. The percentage of $Sr^{2+}$ was increased, the $S_{BET}$ trend to decreased from 55.98 $m^2 g^{-1}$ to 5.11 $m^2 g^{-1}$, which was opposite to the particle size (Figure 3 (c). The large clumps formed and reduced the surface area, which is consistent with a previous finding [32].

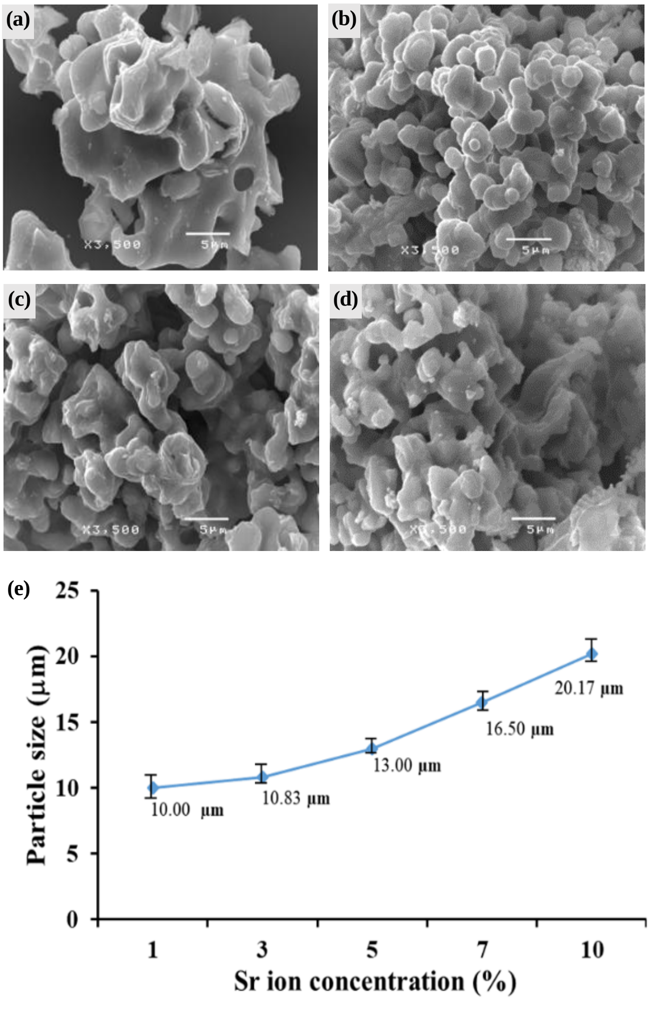

**Figure 3.** SEM image of (a) 1% Sr-CaO, (b) 3% Sr-CaO, (c) 5% Sr-CaO, and (d) 7% Sr-CaO and (e) particle size with strontium concentration (n = 3).

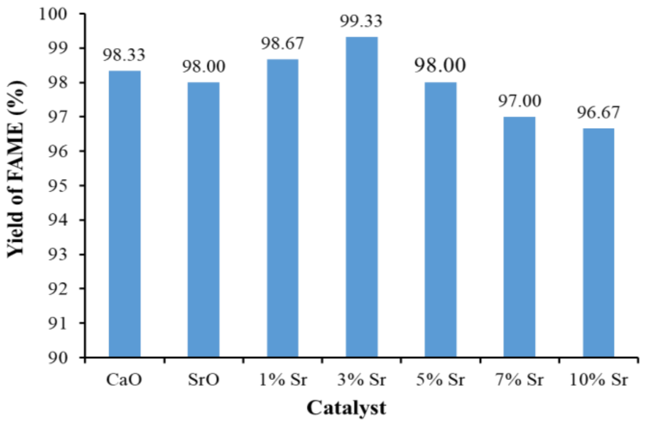

**Figure 4.** Effect of the $Sr^{2+}$ ion loading (%) in the Sr-CaO catalyst on the transesterification reaction of WPCO with methanol in comparison with the SrO catalyst.

### 3.1.6 Basic strength

The basic strength of all the freshly prepared catalysts were in the range $9.8 < H < 15$, and this did not change after storage for 6 month for the SrO and all the Sr-CaO catalysts, but the CaO catalyst decreased to $7.2 < H < 9.8$ upon storage, which might relate to the phase change from CaO to $Ca(OH)_2$ and $CaCO_3$.

## 3.2. Catalytic activity

### 3.2.1 Effect of parameters in transesterification

Of the examined catalysts, the 3% Sr-CaO gave the highest biodiesel conversion level (99.33%), while the other catalysts exhibited a biodiesel conversion level ranging from 96.0% to 98.67% (Figure 4). Increasing the $Sr^{2+}$ loading from 1 to 3 wt% increased the biodiesel conversion level to the highest at 99.33% (3% Sr), and then it decreased down to 96.67% as the $Sr^{2+}$ level further increased up to 10% Sr.

The effect of the methanol:oil molar ratio was studied (1:1 to 9:1) with a fixed reaction temperature of 80°C for 5 h, and a catalyst (CaO or 3% Sr-CaO) concentration of 5 wt% (Figure 5(a)). As the methanol:oil molar ratio was increased from 1:1 to 9:1, the biodiesel conversion level obtained over the CaO catalyst increased from 21.67% (molar ratio 1:1) to a maximum of 98.33% at a 3:1 methanol:oil molar ratio and then slightly decreased with increasing methanol:oil molar ratios. Whereas, for the 3% Sr-CaO catalyst, the biodiesel conversion level increased slightly as the methanol: oil molar ratio increased to 5:1 and then rapidly at 7:1 and was maximal at a 9:1 molar ratio. In accord, it was previously reported that the optimal methanol: oil molar ratio was 3:1 for a pure CaO catalyst for a 5 h reaction at 80°C [28].

The WPCO feed stock had an acid value of 1.2 mg KOH per gram, an acidity level that could reduce the base level of the catalyst at low catalyst loadings and so cause incomplete biodiesel conversion and saponification of the WPCO. To evaluate the effect of the catalyst loading (5 wt% to 20 wt%) on the biodiesel conversion from transesterification of WPCO and methanol, the reaction was performed at 80°C for 5 h at a methanol: oil molar ratio of 9:1 for the CaO and 3% Sr-CaO catalysts, with the results shown in Figure 5(b). Increasing the 3% Sr-CaO catalyst loading from 5 wt% to 20 wt% caused a slight decrease in the biodiesel conversion level, whereas the CaO catalyst gave a low biodiesel conversion at 5 wt% that increased markedly to a maximum level at 10 wt.% and thereafter decreased slightly with further increases in the catalyst loading.

Finally, the effect of the reaction time (1 h to 7 h) was evaluated on the biodiesel conversion level at 80°C, 9:1 methanol:oil molar ratio and 10 wt% catalyst loading, with the results shown in Figure 5(c). For both catalysts, increasing the reaction time from 1 h to 3 h markedly increased the biodiesel conversion level, and this was maximal after 3 h (99.33%) for the 3% Sr-CaO catalyst.

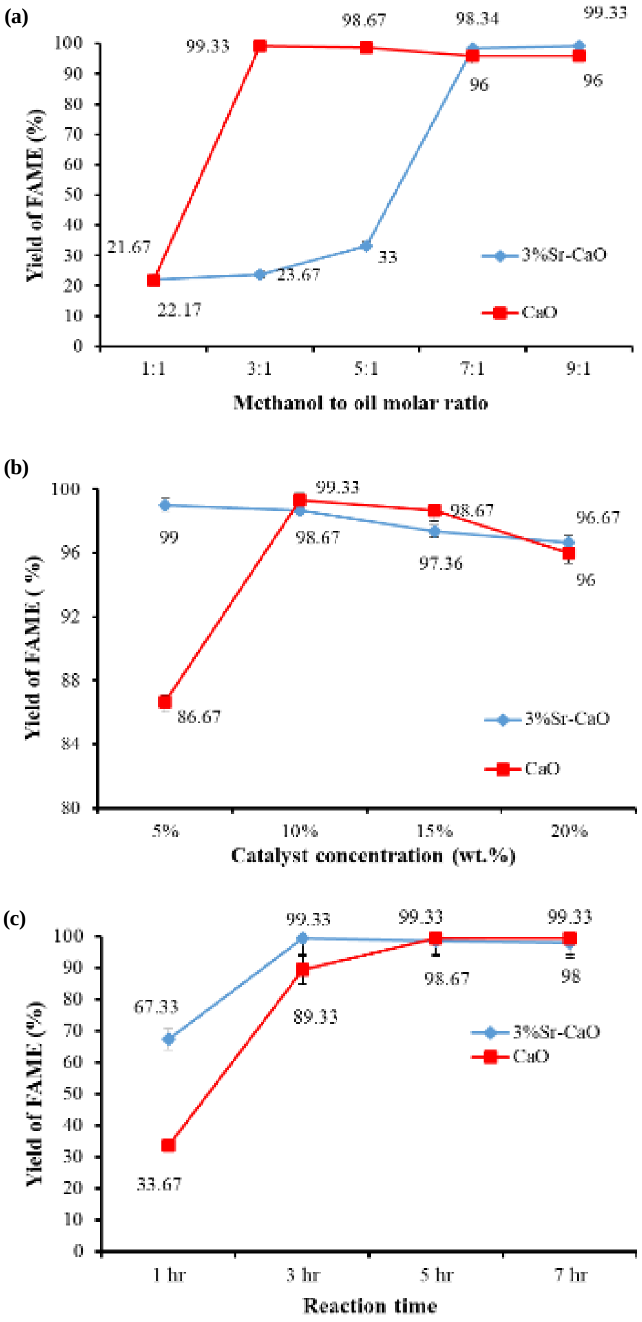

**Figure 5.** Effect of (a) the methanol: oil molar ratio (80°C, 5 h, 5 wt% catalyst loading), (b) the catalyst concentration (80°C, 5 h, 9:1 methanol:oil molar ratio), and (c) the reaction time (80°C, 10 wt% catalyst loading, 9:1 methanol:oil molar ratio) on the biodiesel conversion level in the transesterification of WPCO with the 3% Sr-CaO and CaO catalysts. Data are shown as the mean ± SD (n=3).

## 3.3 Catalyst reusability

The possibility of reuse is one of the advantages of heterogeneous catalysts and so the catalytic activity after up to 10 consecutive transesterification cycles of WPCO and methanol was evaluated for the 3% Sr-CaO and CaO catalysts, with the results shown in Figure 6 [28]. After the reaction, the catalysts were harvested by filtration, cleaned with hexane, and dried at 100°C for 5 h before reuse.

The biodiesel conversion level obtained with the CaO catalyst decreased with each cycle and after five cycles was less 60% and negligible by eight runs. The efficiency of the 3% Sr-CaO did not markedly decrease over the first four cycles and could be reused for more than eight cycles at over a 60% biodiesel conversion level. The decreasing biodiesel conversion level with each use was related to the decreasing catalytic surface area and reduction in the basic strength [25,31]. The SEM image of the reused 3% Sr-CaO catalyst after 10 cycles showed a different surface morphology with the presence of impurities, caused by organic matter from the WPCO (Figure 6(b) and (c)).

## 3.4 Biodiesel properties

The properties of the biodiesel synthesized from the transesterification of WPCO and methanol with the 3% Sr-CaO catalyst under the optimal conditions (methanol:oil molar ratio of 9:1, 10 wt% catalyst loading, 80°C for 3 h) were measured and compared with respect to the EN 14214 and ASTM D 6751 standard methods, with the data shown in Table 1. Biodiesel showed a FAME content of 99.33%, density of 896 kg·m$^{-3}$, and a viscosity at 40°C of 4.55. The cloud point, pour point, and flash point were found at 9°C, -5°C, and 120°C, respectively, and meet the standard biodiesel properties [33]. Thus, this biodiesel would be an effective source of renewable energy.

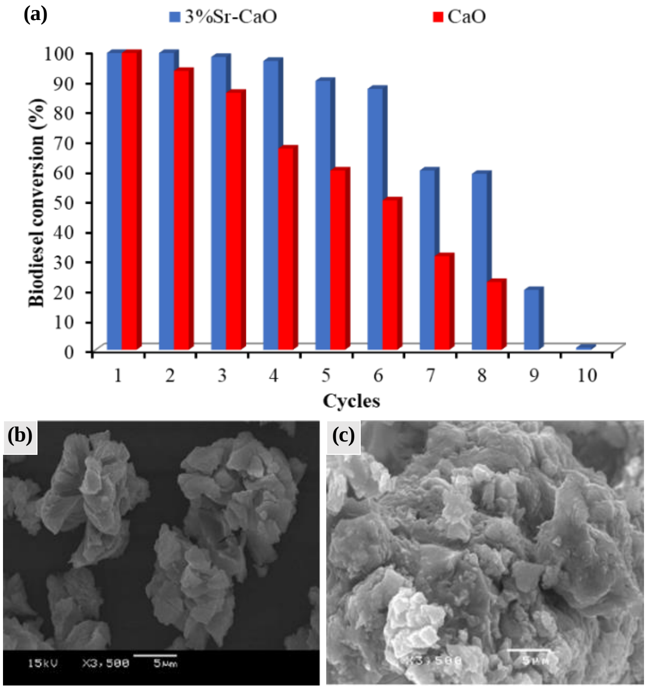

**Figure 6.** (a) Reusability of the 3% Sr-CaO and CaO, (Reaction conditions: methanol: oil molar ratio 9:1, catalyst concentration 5 wt%, reaction time 3 h at 80°C) and the SEM image of reused for 10 cycles of (b) CaO and (c) 3% Sr-CaO catalyst.

**Table 1.** Fuel properties of the prepared FAME (biodiesel) from WPCO and methanol using the 3% Sr-CaO catalyst under the optimal conditions.

| Fuel properties, standard method | Standard value | Biodiesel from wasted cooking oil |
|---|---|---|
| FAME (%) | Min 96.5% | 99.33% |
| Density (kg·m$^{-3}$), ASTM D 1298 | 860 to 900 | 869 |
| Pour point (°C), ASTM D 97 | -15 to -6 | -5 |
| Cloud point (°C), ASTM D 2500 | -3 to 12 | 9 |
| Viscosity at 40°C, ASTM D 445 | 3.5 to 5.0 | 4.55 |
| Flash point (°C), ASTM D 93 | > 93 | 120 |

## 4. Conclusions

A series of Sr-CaO catalysts doped with increasing levels of Sr$^{2+}$ (1 wt% to 10 wt%) was successfully synthesized by co-precipitation and then characterized by TGA, XRD, SEM-EDX, BET, and FTIR analyses, while the basic strength was analyzed by the Hammett indicator method. The TGA results for the non-calcined Sr-CaO catalyst showed two step decomposition and complete conversion from carbonate phase to oxide phase at temperatures higher than 900°C, while the XRD analysis revealed the major peaks of calcium oxide. The SrO peaks at a $2\theta$ of 34.8°and 50° were only found in the 50% Sr-CaO as a $SrCO_3$ impurity. The basic strength ranged from 9.8 < H < 15.0, while the particle sizes were consisted with the concentration of doped Sr$^{2+}$ ions. The increasing Sr$^{2+}$ from 1 wt% to 10 wt% decreased the $S_{BET}$ of the Sr-CaO catalyst from 55.98 m$^2$·g$^{-1}$ (3% Sr-CaO) to 5.11 m$^2$·g$^{-1}$ (10% Sr-CaO). While the increasing Sr$^{2+}$ causes the particle size improved from 10.0 μm (1% Sr-CaO) to 20.17 μm (10% Sr-CaO). The catalytic activity of synthesized Sr-CaO catalysts were evaluated in the transesterification of WPCO and methanol, with the highest FAME conversion level (99.33%) obtained with a methanol:oil molar ratio of 9:1, reaction time of 3 h at 80°C and a 3 wt% catalyst loading. Under these conditions the conditions the 3% Sr-CaO catalyst could be reused for seven cycles at a FAME conversion level of more than 60%. The synthesized biodiesel exceeded the requirement of standards EN 14214 and ASTM D 6751, and so this synthetic biodiesel could be an effective renewable fuel.

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