



# Continuous production of biodiesel in a packed-bed reactor using shell–core structural $\text{Ca}(\text{C}_3\text{H}_7\text{O}_2)_2/\text{CaCO}_3$ catalyst

Li-Shan Hsieh, Umesh Kumar, Jeffery C.S. Wu\*

Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan, ROC

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## ABSTRACT

The continuous production of biodiesel was studied by using a steady-state packed-bed reactor. The shell–core  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_2)_2/\text{CaCO}_3$  solid-base catalyst was prepared with a mechanical strong core of  $\text{CaCO}_3$  for continuous transesterification of soybean oil in a packed-bed reactor. Alcohol–oil ratio, retention time and reaction temperature were evaluated to obtain optimum reaction conditions. The yield of fatty acid methyl esters (FAME, i.e. biodiesel) achieved 95% at the reaction temperature 60 °C, alcohol–oil molar ratio of 30:1 and retention time of 168 min. The reusability of catalyst was checked up to 5 cycles and found negligible decrease in the catalyst activity. Water in the oil can significantly decrease the yield due to the deactivation of  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_2)_2$  and hydrolysis of FAME. The transesterification of soybean oil, canola oil and sunflower oil also was compared with model compound, triolein, using powder  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_2)_2$  in the batch reactor. Although these oils contained different triglyceride mixtures, their FAME yields were comparable. A Langmuir–Hinshelwood rate equation was established for the transesterification of soybean oil with methanol. Regression of experimental data indicated that the transesterification was an endothermic reaction with the enthalpy change of 23,504 J/mol and the activation energy was 42,096 J/mol.

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## 1. 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 fossil diesel [2]. Biodiesel sources do not contain significant amounts of nitrogen and sulfur compounds. Therefore, it has less amounts of  $\text{NO}_x$  and  $\text{SO}_x$  polluting emissions and much cleaner than fossil diesel fuel [3–5]. 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 [6–11]. The fatty acid methyl ester (FAME) is predominantly used as biodiesel.

Commonly, biodiesel has been manufactured by homogeneously catalyzed transesterification of vegetable oil with  $\text{NaOH}$  or  $\text{KOH}$  basic catalysts [12–14]. Base-catalyzed transesterification is much faster than acid-catalyzed. Although homogenous base catalysts have fast reaction rate under mild reacting condition, it is difficult to remove them from reaction mixture or products. In addition, a large amount of water is needed to wash them [15]. This

washing process also is responsible for the waste products of stable emulsion formation and saponification. Homogeneous catalysts also are difficult to separate from glycerol generated as byproduct [16,17].

Solid-base catalysts have great potential for biodiesel processing with reasonable reaction rates under mild conditions. Alumina-supported alkali elements/hydroxides,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{ZrO}_2$ , calcined  $\text{MgAl}$  hydrotalcites, rehydrated hydrotalcites, anion-exchange resin and alkali-exchanged zeolite were used to study biodiesel synthesis utilizing heterogeneous catalytic processes [12,18–26].

Recently, much interest has been taken in  $\text{CaO}$  due to its economy and reactivity for the transesterification of soybean oil and poultry fat [21,27,28]. Some researchers observed that the  $\text{CaO}$  slightly dissolved in methanol during transesterification process. On the other hand,  $\text{CaO}$  was transformed into calcium diglyceride by combining with glycerol during transesterification of soybean oil with methanol [28,29]. The leaching of the solid-base catalyst occurred simultaneously with the active phase transformation. The sensitivity of  $\text{CaO}$  to atmospheric  $\text{CO}_2$  to form  $\text{CaCO}_3$  is the major disadvantage because  $\text{CaCO}_3$  is inactive for transesterification reactions. The solid phase  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_2)_2$  catalyst has overcome  $\text{CaO}$  deactivation and separation problem [29]. However, the mechanical strength of  $\text{CaO}$  particle is weak so it would collapse in a packed-bed reactor. On the other hand,  $\text{CaCO}_3$  particle is mechanically strong to be used inside a packed-bed reactor.

\* Corresponding author at: Department of Chemical Engineering, National Taiwan University, No. 1, Section 4, Roosevelt Road, Taipei 10617, Taiwan, ROC. Tel.: +886 223631994; fax: +886 223623040.

E-mail address: [cswu@ntu.edu.tw](mailto:cswu@ntu.edu.tw) (J.C.S. Wu).

The objective of this study was to demonstrate a continuous biodiesel production process. A shell–core  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$  chunk with a mechanically strong  $\text{CaCO}_3$  core can facilitate low-pressure drop in packed-bed reactor. The transesterifications of soybean oil, canola oil, sunflower oil and model compound, triolein, were compared to reveal any effects of different triglyceride mixtures. The influence of retention time, temperature and methanol-to-oil ratio, was investigated to achieve the optimized reaction conditions. Finally a Langmuir–Hinshelwood model also was established to correlate the experimental result.

## 2. Experimental

### 2.1. Materials and characterization

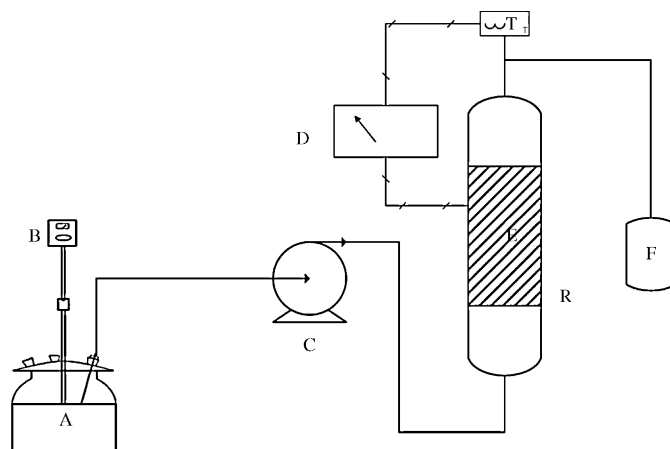
Soybean oil, canola oil and sunflower oil (all FFA contents <0.5%) were obtained from Uni-President Company, Taiwan and used directly without pretreatment.  $\text{CaO}$  (98%) and 2-propanol (>99.8%) were purchased from Sigma–Aldrich. Triolein ( $\text{C}_{57}\text{H}_{104}\text{O}_6$  >97%) and chemical grade methanol (>99.8%) were purchased from Fluka.

Shell–core  $\text{CaO}/\text{CaCO}_3$  catalyst was prepared by calcining  $\text{CaCO}_3$  chunks (5–6 mesh size, ~4 mm) in a helium atmosphere at  $900^\circ\text{C}$  for 1.5 h at heating rate of  $6^\circ\text{C}/\text{min}$ . An outer layer  $\text{CaO}$  was formed after  $\text{CO}_2$  was released from the surface of  $\text{CaCO}_3$  chunks with mechanically strong  $\text{CaCO}_3$  core. This  $\text{CaO}/\text{CaCO}_3$  chunk was refluxed in 50% glycerol/methanol mixture with continuous stirring for 2 h to obtain the outer layer of calcium diglyceride ( $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$ ). Then, the white chunks were thoroughly washed with methanol and dried in air. The same procedure also was applied  $\text{CaO}$  to prepare the powder-form  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$  catalyst [29]. The basic strength of  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$  was determined by pH indicators within the color changes between phenolphthalein and 2,4-dinitroaniline. The base density of catalyst was measured by acid–base back titration with standard solution of benzoic acid.

X-ray diffraction (XRD) patterns of the catalysts were obtained using a Philip X'Pert diffractometer. The X-ray (wavelength  $\lambda = 1.5405 \text{ \AA}$ ) tube was equipped with copper target operated at 40 kV and 30 mA. The scanning rate was  $3^\circ/\text{min}$  from  $5^\circ$  to  $50^\circ$ . Surface area measurements were performed by  $\text{N}_2$  adsorption at room temperature using a Micromeritics ASAP 2000/C5-05 instrument. Prior to  $\text{N}_2$  adsorption, the samples were degassed in low pressure (10 mm Hg) at room temperature and  $210^\circ\text{C}$ . Surface areas were calculated using the Brunauer–Emmett–Teller (BET) equation over the relative pressure range  $P/P_0$  between 0.02 and 0.22, where a linear relationship was maintained. Thermogravimetric analyses (TGA) of samples were done on a Netzsch, STA 409CD Thermogravimetric analyzer equipped with a mass spectrometer (Balzers, QMA 400) in helium atmosphere at a heating rate of  $10^\circ\text{C}$  per min.

### 2.2. Transesterification of oil

The reactions were carried out in a cylindrical reactor with capacities of ca. 60 ml stainless steel tube (1.71 cm inside diameter with 26.0 cm in length). The schematic diagram of the experimental setup is shown in Fig. 1. The soybean oil and methanol were placed in a four-neck flask, mixed by mechanical stirring and then fed into the reactor by an HPLC pump. The molar ratio of methanol to oil ranged 6–36. The tubular reactor was wrapped with heating tape. Temperature of reaction was kept below the boiling point of methanol ( $\sim 65^\circ\text{C}$ ) to prevent two-phase flow. The reactor temperature was monitored by thermocouples placed at the center of the tubular reactor. With this arrangement, the reaction temperature could be controlled with a precision of  $1^\circ\text{C}$ . The retention time of the reaction was adjusted by regulating the flow rate of the



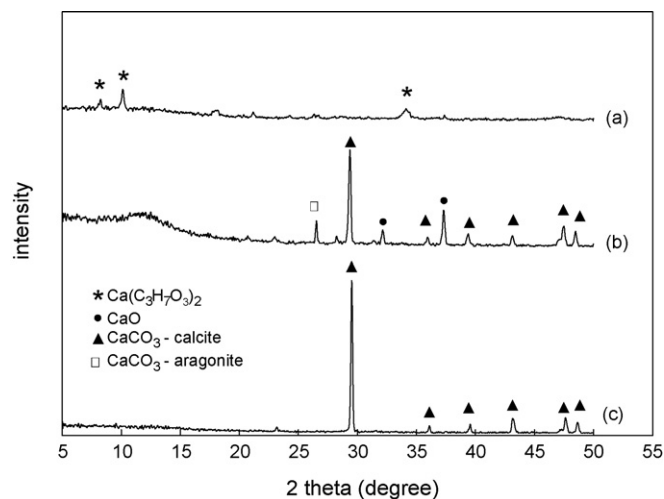
**Fig. 1.** Schematic diagram of packed bed reactor where A= four-neck flask, B= mechanical stirrer, C= HPLC pump, D= temperature controller, E= heating tape, F= sample collector, R= reactor, and T= thermocouple.

reaction mixture. Samples were collected periodically in glass vials placed at the reactor outlet, and analyzed with GC. After reaction, reactants and products of soybean oil, canola oil, sunflower oil and triolein were diluted with isopropanol (dilution factor 50) and then analyzed with a Hewlett Packard gas chromatograph (HP 6890) equipped with a HP-INNOWAX capillary column (0.32 mm ID and 30 m long) and flame ionization detector. The yield of biodiesel was calculated by the summation of all FAMES divided by the weight of oil.

## 3. Results and discussion

### 3.1. Characteristics of catalyst

The calcination of the  $\text{CaCO}_3$  powder and chunks gave  $\text{CaO}$  and  $\text{CaO}/\text{CaCO}_3$  respectively, at  $900^\circ\text{C}$  under helium atmosphere. The  $\text{CaO}$ , on reaction with glycerol, yielded  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$  [29,30]. The  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$  chunks contained thin layers of  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$  on their surface. That  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$  layer was carefully peeled off and ground for XRD analysis as shown in Fig. 2. Calcium diglyceride formation on  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$  catalyst was observed in Fig. 2(a) with the presence of characteristic peaks of  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$  at  $2\theta$  angles of  $8.2^\circ$ ,  $10.1^\circ$ ,  $34.1^\circ$  [29]. The core of the catalyst had



**Fig. 2.** XRD pattern of  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$ : (a)  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$  (after peeling  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$  from  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$ ), (b)  $\text{CaO}/\text{CaCO}_3$  (after calcination at  $900^\circ\text{C}$ ) and (c)  $\text{CaCO}_3$ .

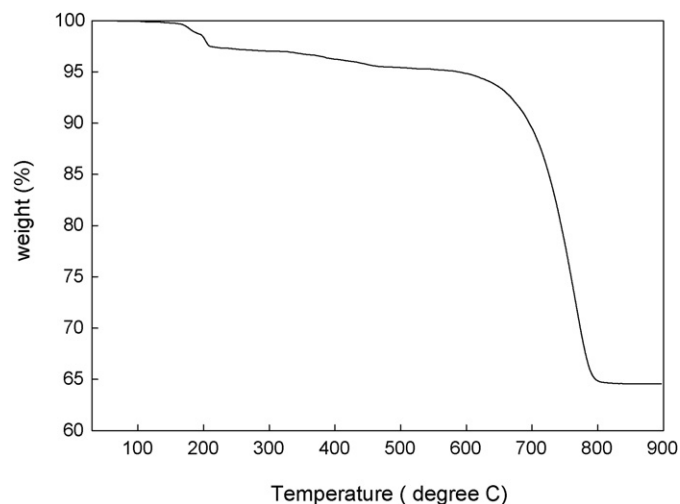


Fig. 3. TGA spectra of  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$  catalyst under He flow.

only the characteristic peak of calcium carbonate. After calcination, the calcite form slightly changed to aragonite and CaO. The XRD diffraction peaks at  $32.2^\circ$  and  $37.3^\circ$ , shown in Fig. 2(b), are the characteristics peaks of CaO, generated after calcination of  $\text{CaCO}_3$  for 1.5 h indicating the surface formed a CaO structure. No XRD diffraction peak was observed for  $\text{Ca}(\text{OH})_2$ . For comparison, Fig. 2(c) shows that the original  $\text{CaCO}_3$  contained only calcite form.

The TGA-mass analysis of catalyst is shown in Figs. 3 and 4. Fig. 3 shows the weight loss of the  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$  chunks up to  $900^\circ\text{C}$ . Fig. 4 shows that the  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$  had three derivatives of cracking  $\text{C}_3\text{H}_7\text{O}_2$ ,  $\text{C}_3\text{H}_7\text{O}_3$  and  $\text{C}_3\text{H}_8\text{O}_3$  near  $450^\circ\text{C}$ . The  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$  catalyst decomposed in three steps during the thermal analysis. Initial 1.5% weight loss around  $200^\circ\text{C}$  was due to loss of water and  $\text{CO}_2$ , which were physically adsorbed on the surface of the catalyst. The second decomposition step was at around  $450^\circ\text{C}$ . A loss of 2.9% weight was due to the elimination of glyceride group from the  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$ . The third decomposition step started at  $600^\circ\text{C}$  and ended at  $800^\circ\text{C}$ .  $\text{CO}_2$  was released and left 64% weight of CaO as final residue. The same TGA-mass pattern was observed for powdered  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$  with 31% final residue of CaO. Powdered  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$  and chunked  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$  degassed at  $210^\circ\text{C}$ , had surface areas of  $153.5\text{ m}^2/\text{g}$  and  $3\text{ m}^2/\text{g}$ , respectively. After degassing at room temperature, powdered  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$  and chunked  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$  had surface areas of

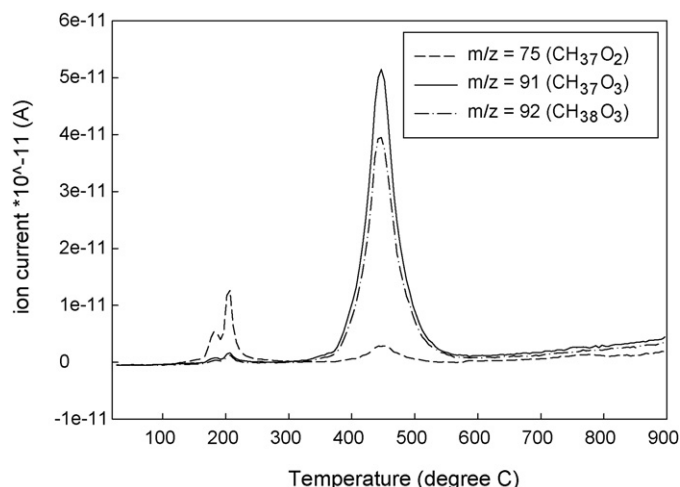


Fig. 4. TGA-mass spectra of  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$  catalyst under He flow.

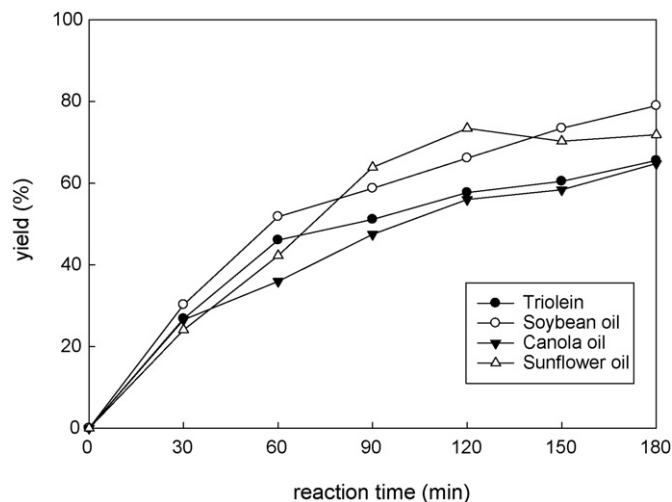


Fig. 5. Batch transesterification with methanol-to-oil molar ratio 30:1, 1 wt.%  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$  catalyst loading and temperature at  $50^\circ\text{C}$ .

$4.33\text{ m}^2/\text{g}$  and  $0.15\text{ m}^2/\text{g}$ , respectively. Catalysts degassed at  $210^\circ\text{C}$  had higher surface areas due to the removal of the extra deposited glycerol.

Transesterification potential is directly proportional to the basic strength and base density of solid-base catalyst. The higher the basic strength and base density, the higher activity and rate would be [31]. The basic strength of  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$  is between H<sub>9.3</sub> and 15. The base density is  $0.19\text{ mmol OH}^-/\text{g}$ .

### 3.2. Comparison between different oils and model compounds

Natural oils have special composition of various fatty acids and may have different activities for transesterification reactions. The comparative activity was checked for soybean oil, canola oil, sunflower oil, and model compounds of triolein using  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$  catalyst in a batch reactor. Figs. 5 and 6 show the yields of soybean oil, canola oil, sunflower oil, and model compounds of triolein with a fixed methanol-to-oil ratio of 30:1 and 1 wt.%  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$  catalyst at  $50^\circ\text{C}$  and  $60^\circ\text{C}$ , respectively. At  $50^\circ\text{C}$ , the soybean oil had the best yield of 75% followed by sunflower oil at 70%. Canola oil and triolein had 63% yields after 3 h reaction time. The initial rate of sunflower oil was slow so that its yield was lower than others before 30 min reaction time. But its rate sustained while the rates

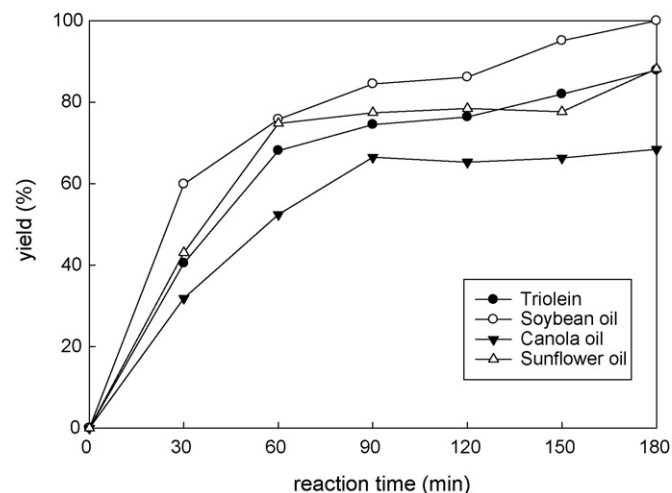


Fig. 6. Batch transesterification with methanol-to-oil molar ratio 30:1, 1 wt.%  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$  catalyst loading and temperature at  $60^\circ\text{C}$ .

**Table 1**

Effect of methanol-to-oil molar ratio on transesterification of soybean oil catalyzed by  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$  in the packed-bed reactor.

Methanol-to-oil molar ratio	Yield (%)
6	3.6
12	7.8
18	9.8
24	11.7
30	13.9
36	14.9

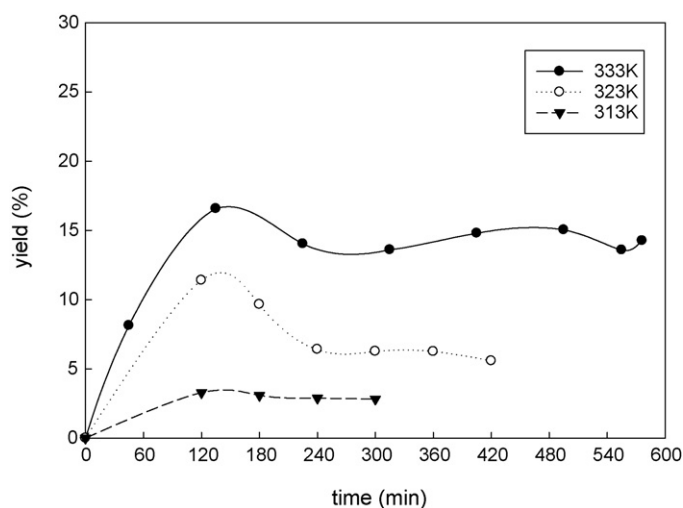
Reaction temperature: 60 °C; retention time: 16.8 min.

of soybean oil and triolein decreased around 60 min reaction time. Thus the yield of sunflower oil was higher than those of soybean oil and triolein. However, after 90 min, the final rate of sunflower oil quickly decreased to near zero so that its yield leveled off. Fig. 6 shows that initial reaction rates were faster at 60 °C. By the end of a 3 h reaction, soybean oil reached 100% yield, and sunflower oil and triolein had nearby 80% yields. But canola oil had no significant increment in yield with rise in temperature. At near 60 min reaction, the rate of sunflower oil was quickly decreased to near zero thus its yield leveled off. Although natural oils contain different amounts of triglyceride mixture, their transesterifications are, by and large, similar to single compound, triolein. Soybean oil had the highest amount of short carbon chains of fatty acids (C16:0) in comparison to canola oil, sunflower oil and triolein. These short carbon chains of fatty acids have less steric hindrance in comparison to long carbon chains of fatty acids and, therefore, have more possibility of contact with catalyst. Consequently, soybean oil gave the highest FAME yield among these oils.

### 3.3. Transesterification of soybean oil in the packed-bed reactor

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 of methanol-to-soybean oil ratio was investigated from 6:1 to 36:1. Table 1 lists the biodiesel yields for the various molar ratios of methanol to soybean oil at a flow rate of 1 ml/min (retention time 16.8 min) at 60 °C in the packed-bed reactor, which was filled with  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$  catalyst. The initial increment from 6:1 to 12:1 gave a onefold increase in yield of transesterification (3.54–7.78%). The viscosity of soybean oil reduces on the increase in methanol amount. According to the Le Chatelier's principle, the increase in methanol amount was responsible for the reduction on backward reaction and increased product yield. The increase in transesterification became slower upon further increase in methanol-to-oil 18:1 and 24:1 ratio and leveled off at 30:1 to 36:1 methanol-to-oil ratio (yield 13.97–14.94%). Consequently, the methanol-to-oil ratio of 30:1 was further studied in the transesterification of soybean oil under our experimental conditions.

The effects of temperature on the conversion of oil to biodiesel was studied by varying the temperature from 40 °C to 70 °C and keeping fixed 30:1 methanol-to-oil molar ratio with 1 ml/min flow (i.e. retention time 16.8 min). Fig. 7 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, and the yields reached steady state in about 120–180 min reaction time. At 40 °C, the least yield (ca. 4%) was observed. At 50 °C, the yield was higher (12%) up to the initial 2 h reaction and then decreased to 7% and became steady after 4 h reaction time. At 60 °C, the reaction conversion was highest (15%). Increasing the temperature to 70 °C, a fluctuation was



**Fig. 7.** Effect of temperature on the yield of transesterification of soybean oil with  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$  in the packed-bed reactor (methanol/oil = 30, flow rate = 1 ml/min, retention time = 16.8 min, and 30 ml catalyst).

observed with lower yield (not shown in Fig. 7). 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 soybean oil in the packed-bed reactor.

Table 2 lists the relationship of retention times and yields. The retention time of the packed-bed reactor was calculated by the void volume of the catalyst bed divided by the flow rate. The biodiesel yields increased with retention time. A maximum of 95% yield was achieved at 168 min retention time with 30:1 methanol-to-oil ratio at 60 °C.

The reusability of the  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$  catalyst was studied in a circulated packed-bed reactor. The reaction was run for 6 h at 60 °C with 30 ml catalyst bed, 30:1 methanol-to-oil ratio and, finally, the yield reached 95%. The catalyst and reactor were washed thoroughly with isopropanol and repeated the above operation again. The reusability of catalyst was checked up to 5 cycles and found negligible decrease in the catalyst activity.

### 3.4. Effect of water

Usually, waste oils contain high contents of free fatty acid and water. The water content should be less than 0.06 wt.% for liquid phase transesterification with a base catalyst [32,33]. The effect of water on transesterification was examined with reaction mixture containing 5 wt.% water. The test run was carried out by 1 ml/min flow rate with 30:1 methanol-to-oil ratio in a half-height of catalyst bed at 60 °C. The water was found to have a significant impact on the base catalyst. The FAME yield decreased from 5.2%

**Table 2**

Effect of retention time on yields on the transesterification of soybean oil catalyzed by  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$  in the packed-bed reactor.

Retention time (min)	Yield (%)
5.3	4.4
6.4	3.1
16.8	13.9
24.0	43.0
33.6	58.6
129.4	77.0
168.2	95.0

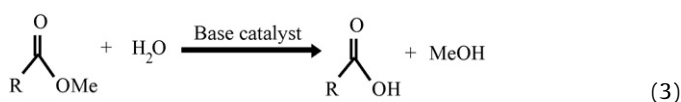
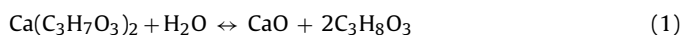
Reaction temperature: 60 °C; methanol-to-oil molar ratio = 30:1.

**Table 3**  
Kinetic parameters of the Langmuir–Hinshelwood rate equation in the transesterification of soybean oil with methanol.

Temperature	$k \left[ \frac{\text{L}^2}{\text{gCa}(\text{C}_3\text{H}_7\text{O}_2)_2 \cdot \text{mol} \cdot \text{h}} \right]$	$K$	$K_A$ [L/mol]	$K_B$ [L/mol]	$K_C$ [L/mol]	$K_D$ [L/mol]	$R^2$
60 °C	0.0048	3.50	1.20	0.011	0.23	0.21	0.90
50 °C <sup>a</sup>	0.0030	2.69	1.69	0.012	0.26	0.26	–
40 °C	0.0018	2.02	2.46	0.014	0.30	0.34	0.70

<sup>a</sup> Interpolation using the experimental data at 40 °C and 60 °C.

to less than 2.3% upon introducing 5 wt.% water, i.e., more than 40% loss.  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_2)_2$  can be decomposed to CaO and glycerol on reaction with water, as shown in Eq. (1). CaO is further reacted with water and becomes calcium hydroxide in Eq. (2). Therefore, water was responsible for the loss of active sites ( $\text{Ca}(\text{C}_3\text{H}_7\text{O}_2)_2$ ) on the catalyst. In addition, with the help of base catalyst, the FAME can be hydrolyzed with water to generate free fatty acid (FFA) and methanol resulting in further decrease of yield as shown in Eq. (3).



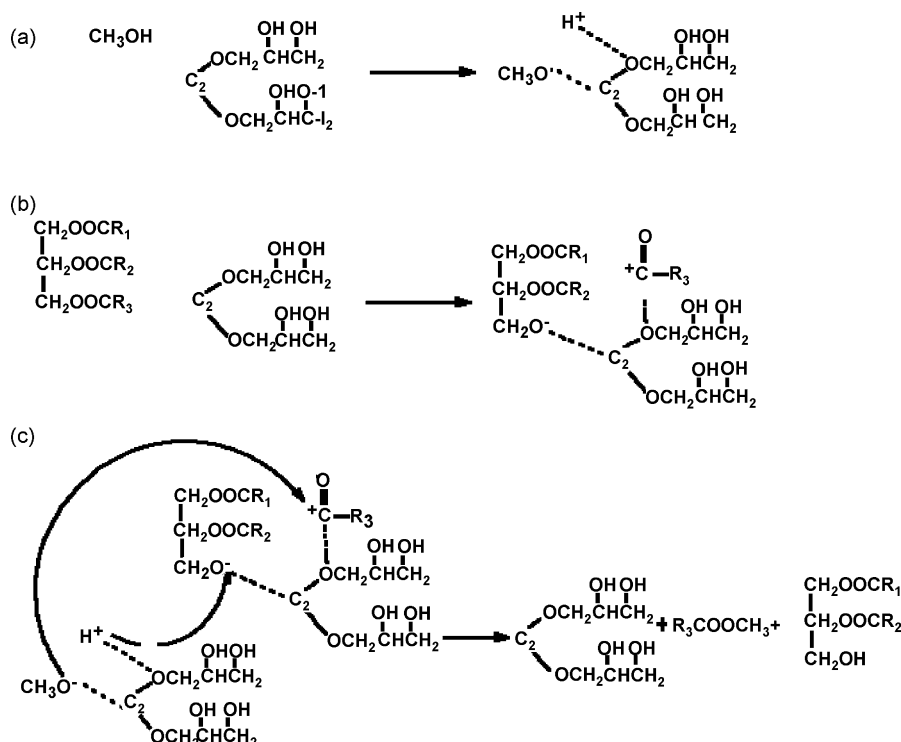
### 3.5. Rate equation and reaction mechanism of transesterification

The Langmuir–Hinshelwood model was used to derive a rate equation for transesterification of soybean oil in the packed-bed reactor. According to this model, the reaction has three steps, adsorption of reactants, surface reaction and desorption of products. Eq. (4) describes the overall reaction of triglyceride (A) and methanol (B) to form three FAME (C) and glycerol (D). The elemental steps of transesterification are proposed in Eqs. (5)–(11). Both triglyceride and methanol are adsorbed on the same active site of

the  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_2)_2/\text{CaCO}_3$  catalyst. No deactivation of the catalyst is assumed. Initially, the triglyceride (A) and methanol (B) adsorbed on the active site of catalyst, then triglyceride reacted with one molecule of methanol to generate one FAME (C) and diglyceride (E). The diglyceride further reacted with methanol to generate one monoglyceride (F) and one more FAME (C). Finally, the monoglyceride reacted with methanol to generate the last FAME (C) and glycerol (D). FAME (C) and glycerol (D) eventually desorbed from the active sites.



$$r_c = \frac{kC_B^{-2}(C_A C_B^3 - C_C^3 C_D / K)}{(1 + K_A C_A + K_B C_B + K_C C_C + K_D C_D)^2} \quad (12)$$



**Scheme 1.** Proposed reaction mechanism of the transesterification of triglyceride with methanol catalyzed on  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_2)_2$  base catalyst.

Noureddini and Zhu showed that the reaction of triglyceride with methanol was slower than those of the diglyceride and monoglyceride [34]. Thus, Eq. (7) is assigned to be the rate-limiting step of the transesterification. After a mathematical procedure, Eq. (12) was derived to be the rate equation. The kinetic parameters were obtained from Matlab regression using experimental data. Table 3 summarizes the kinetic parameters, including rate constant ( $k$ ), reaction equilibrium constant ( $K$ ) and adsorption equilibrium constants ( $K_A$ ,  $K_B$ ,  $K_C$  and  $K_D$ ) of four species. The values of these constants are within the reasonable range indicating that the Langmuir–Hinshelwood model was appropriate to describe the esterification reaction rate of soybean oil with methanol.

From the rate constants ( $k$ ) in Table 3, the activation energy of the catalytic transesterification of soybean oil can be calculated by Arrhenius equation ( $k = A_0 \cdot e^{-E_a/RT}$ ). The activation energy was estimated to be 42,096 J/mol and pre-exponential term ( $A_0$ ) 19,260. The values of reaction equilibrium constant ( $K$ ) increase with temperature indicating endothermic reaction in nature. The reaction enthalpy also was calculated to be 23,504 J/mol based on thermodynamics equation ( $K = K_0 \cdot e^{-\Delta H/RT}$ ). Our reaction enthalpy was close to the value in the literatures. Noureddini and Zhu [34] reported 5267 cal/mol (22,016 J/mol) enthalpy for transesterification reaction. Freedman et al. [35] obtained a value of 3895 cal/mol (16,281 J/mol). In addition, the values of adsorption equilibrium constants ( $K_A$ ,  $K_B$ ,  $K_C$  and  $K_D$ ) decreased with increase in temperature due to the exothermic adsorption process. The calculated rate of methyl ester at 50 °C (i.e., 0.00483 mol/g  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2 \cdot \text{h}$ ) was comparable with the experimental results (0.00418 mol/g  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2 \cdot \text{h}$ ).

The reaction mechanism of transesterification of soybean oil with methanol on  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$  is described in Scheme 1. The  $\text{CaO}$  of  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$  acted as a Brønsted base, which was the source of basic active site. Therefore, the oxygen in the glyceride bonded directly with the calcium in the  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$  interacts with methanol, and extracts a proton ( $\text{H}^+$ ) from the methanol to form methoxide ion ( $\text{CH}_3\text{O}^-$ ). The methoxide ion interacted with neighboring calcium as shown in Scheme 1(a). Similarly the triglyceride interacts with  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$  to form the intermediate species as shown in Scheme 1(b). Then, these two intermediate species interacted with each other to form fatty acid methyl ester (FAME) and diglyceride (Scheme 1(c)). The repetitions of the reaction finally generated the three moles of FAME and one mole of glycerol.

#### 4. Conclusions

A  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2$  catalyst was synthesized and used for the batch transesterification of variety of oils, included canola and sunflower oils. Soybean oil gave the maximum transesterification yield due to short carbon chain of fatty acid. A shell–core  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$  catalyst was successfully synthesized by the calcination of  $\text{CaCO}_3$  particle followed by glyceride reaction. This catalyst was employed in a continuous flow packed-bed system, in which the products and the catalyst could be separated easily. An increase in the feed ratio of methanol on soybean oil can improve yield, but eventually reaches a limit. The  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$  catalyst produced a 95% FAME yield of soybean oil at 60 °C with 30:1 methanol-to-soybean oil molar ratio with the 168 min retention time. The reusability test of the catalyst  $\text{Ca}(\text{C}_3\text{H}_7\text{O}_3)_2/\text{CaCO}_3$  was done up to 5 cycles, and no significant decrease in reaction yield was observed. However, water in the oil had a significant impact on catalytic transesterification using base catalyst. Transesterification on the solid catalyst was described appropriately by a Langmuir–Hinshelwood rate equation. The regression results from the experimental data pointed out that the transesterification was an endothermic reaction with the enthalpy change of 23,504 J/mol and activation energy 42,096 J/mol.

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