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Algae derived biodiesel using nanocatalytic transesterification process



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ABSTRACT

This work investigates the nanocatalytic biodiesel production from algae (*Nannochloropsis* sp.). The hydrothermal synthesis route was used in this study to produce nano $\text{Ca}(\text{OCH}_3)_2$ (calcium methoxide) as a model catalyst. The effect of the main reaction parameters i.e. catalyst dosage, temperatures under constant pressure, methanol molar ratio and reaction time on the yield of FAME (fatty acid methyl ester) were examined. Kinetic study of biodiesel synthesis from crude microalgae oil using nanocatalytic transesterification reaction was appraised. The results indicate that CH_3O^- species (a cluster of tiny plate-like architectures) in $\text{Ca}(\text{OCH}_3)_2$ catalyst, and acted as main active sites for transesterification process. In addition, $\text{Ca}(\text{OCH}_3)_2$ catalyst has excellent catalytic performance in production of biodiesel. The highest FAME yield of 99.0% was obtained over 3 wt.% of $\text{Ca}(\text{OCH}_3)_2$ catalyst loading at methanol to oil molar ratio of 30:1 and reaction time of 3 h at 80 °C. Moreover, the catalyst displays a good stability and reutilization. A satisfactory FAME yield of 96% was achieved after use for five consecutive cycles without significant deactivation. The activation energy (E_a) of the transesterification reaction of crude *Nannochloropsis oculata* oil with methanol over $\text{Ca}(\text{OCH}_3)_2$ nanocatalyst was obtained as 58.62 kJ mol⁻¹. The results revealed that the yield of methyl esters obtained from algae-based triglycerides was follows a pseudo first order mechanism for the forward reaction. These results suggest that the nanocatalyst is a promising for a green biodiesel production process from algae.

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1. Introduction

One of the major environmental problems associated with the consumption of fossil fuel resources is global warming and climate change. Hence, many of the developed country including Italy, USA, France and Brazil have taken initiative to enhance the alternative energy research. It was reported that the reserves of coal, oil and natural gas will be exhausted by 122, 42 and 60 years, respectively (Islam et al., 2014). Therefore, researchers have directed toward the alternative renewable

energy sources to reduce and replace petroleum derived diesel fuel.

Recently, biodiesel is made entirely from a wide spectrum of feedstocks i.e. edible (virgin oil) non-edible or waste cooking, waste frying, animal or fish waste and microalgae oils, and its merits as an alternative, renewable energy source, biodegradable, environmental friendly (Birla et al., 2012; Palligarnai and Michael, 2008). Edible oil contributes 95% of the feedstock constituent for biodiesel production (Hassan and Vinjamur, 2014). Nevertheless, the use of food-based

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feedstock extensively for production of biodiesel is shrinking arable land availability and the worldwide concern over the fuel versus food debate. The shortage of the edible oil in many developing and undeveloped countries remains a question mark to further production of biodiesel from edible oils (Hassan and Vinjamur, 2014). Hence, it does not seem to be an ideal justification to divert edible oil to sustainable biofuels production. On the other hand, discovering the potentials of the non-edible feedstocks such as *Jatropha curcas* and *Pongamia pinnata* to be high efficient for making biodiesel (Boucher et al., 2008). Apart from this, the other plant species including microalgae oil also indicated as a novel feedstock, which have a high potential to convert biodiesel with high yield (Nautiyal et al., 2014). Newly, algae-based lipid for biodiesel is in the beginning phases of research, however it has posed enormous prospective to offer alternative new generation feedstock (Lam et al., 2012). The advantage of the algae based feedstock is that the lipid productivity can be 15–300 times (respect to the dry weight of biomass) larger than that derived from plant (Lam et al., 2012; Lee et al., 2010). Nonetheless, the optimization of important parameters i.e. light, pH, temperature, nutrients in their cultivation and also the extraction of oil for a high yield with low cost is currently a challenge (Lam et al., 2012; Lee et al., 2010; Lam and Lee, 2012).

The use of different supported earth metal oxide, zirconia and zeolite based oxide catalysts have been reported in the literature (Xie and Zhao, 2014; Xie et al., 2011; Xie and Fan, 2014; Xie and Zhao, 2013). Generally, most of these catalysts have been posed favorable outcomes with high conversion of biodiesel. It may be mentioned that the calcium derived based were still remain to be the most potential catalyst as they are abundance, inexpensive, show low methanol solubility and also non-toxic among the catalysts studies recently.

A noteworthy amount of research work has been conducted on the kinetic reaction for producing biodiesel. Uzun et al. (2012) reported the reaction kinetic of base catalyzed transesterification using waste frying oil with excess methanol. Reaction kinetics of palm oil based biodiesel has been reported recently by Shahbazi et al. (2012). The activation energies of transesterification on different feedstocks for biodiesel production has been reported by Asakuma et al. (2009) using the quantum computation chemistry. The kinetic approach of algae (*Nannochloropsis oculata*) derived biodiesel using $\text{Ca}(\text{OCH}_3)_2$ nanocatalyst was reported in this study. The effect of reaction parameters on biodiesel yield and the rate constant for the $\text{Ca}(\text{OCH}_3)_2$ catalyzed transesterification of *N. oculata* were evaluated. Finally, the catalyst reusability in the transesterification of microalgae *N. oculata* to biodiesel was also studied.

2. Experimental

2.1. Materials

Pure microalgae *N. oculata* strain was obtained from AlgaeTech Sdn. Bhd., Malaysia. Calcium oxide (CaO) >90% was purchased from SigmaAldrich Chemical. All other reagents used for this study were analytical grade.

2.2. Microalgae biomass preparation

500 ml of decontaminated microalgae *N. oculata* strain further propagation using photoautotrophic cultivation method. The culture was flocculated, washed and triturated to collect

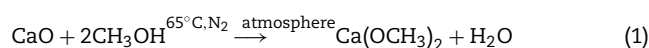
microalgae biomass. The lipid extraction was performed using modified bligh and dyer method (Nautiyal et al., 2014). The microalgae were subjected to pulverization in mortar for cell disruption follow by mesh sieving. The resultant powdered biomass was placed in the 500 ml conical flask along with methanol–chloroform (1:2 v/v) solvents. The contents in the flask were stirred with the help of magnetic stirrer at a particular speed. In order to prevent any losses of hexane and methanol due to evaporation the set up was completely covered with aluminum fold. After the stipulated time, the stirring was stopped and the products were filtered. The crude lipid was concentrated, and then stored in a dark, well close, glass bottle in a freezer for transesterification reaction.

2.3. Crude lipid analysis

The samples were analyzed by the method described elsewhere (Arifin et al., 2009). Conventional sodium hydroxide was used for converting fatty acid to methyl ester. After the stipulated of the reaction, the products were allowed to settle into two layers. The upper layer comprised solvent with biodiesel was transferred into a micro-centrifugal. The analysis of biodiesel was performed by using GC-2010 series Gas chromatograph coupled to a mass spectrometer (Shimadzu GCMS-QP2010). Moreover, the contents of moisture, free fatty acid and dried ash from crude lipid were determined using previous reported method (Andrikopoulos et al., 2001).

2.4. Catalyst preparation

$\text{Ca}(\text{OCH}_3)_2$ catalyst was synthesized by refluxing calcium oxide (CaO) with dehydrated methanol at 65 °C in condition of N_2 flow for 8 h. The following Eq. (1) states the reaction:



The experiment was performed in a reactor having a capacity of 500 ml. In a typical preparation process, CaO (10 g) was suspended into 300 ml of methanol. The methanol was then distilled until dryness using a rotary evaporator. The catalyst was powdered with mortar and pestle and sieve with 250 μm to obtain micron sized catalyst for the reaction.

2.5. Catalyst characterization

The X-ray diffraction (XRD) of the catalyst was recorded by diffractometer (XRD-6000, Shimadzu) using $\text{CuK}\alpha$ radiation at scanning rate of 2°min^{-1} . The total surface area (S_{BET}), total pore volume ($\text{cm}^3 \text{g}^{-1}$) and average pore size (nm) of the catalyst were evaluated by Sorptometer (1900 series, Thermo Finnigan Sorptomatic). Surface area was calculated using Brunauer–Emmett–Teller (BET) equation form the adsorption/desorption branch of the isotherm in a relative pressure range of 0.07–0.3. Whereas, the pore size distribution was determined from desorption branches derived from Barrett–Joyner–Halenda (BJH) plot at -196°C temperature. Thermogravimetric (TGA) and differential thermal analyses (DTA) were performed using a Mettler Toledo thermogravimetric analyzer. The heating was carried out in a normal air flow and maintained at 100ml min^{-1} . The heating rate was $10^\circ\text{C min}^{-1}$. The analyses of the catalyst were determined using attenuated total reflection-Fourier transform-infrared spectroscopy (ATR-FTIR). Infrared absorption spectra were

obtained using a FTIR spectrometer (PerkinElmer (PC) Spectrum 100 FTIR spectrometer) with He–Ne laser source at N₂ temperature. The average spectrum was recorded from triplicate analysis ranging from 400 to 4000 cm⁻¹ at a resolution of 4 cm⁻¹. Scanning electron microscopy (SEM) was taken with a JOEL JSM6700F Field Scanning Electron Microscope (FESEM). To protect the induction of electric current, the catalyst was coated with Au (gold) by a sputter coater with maximum operating voltage used was 25 kV. Hitachi H7100 Transmission Electron Microscopy (TEM) was used to measure the particle size of the catalyst with a voltage of 200 kV.

2.6. Transesterification reaction

The experiments were performed using a glass-type instrument with water-cooled reflux condenser and stirrer. A thermocouple was used to determine the temperature of the reaction. Transesterification was carried out with different methanol/oil ratio (10–60 molar ratios), catalyst concentrations (3–15 wt.%), temperatures ranging from 50 to 80 °C and reaction times (30–240 min). To start each experiment, a typical amount of oil, catalyst and methanol were added together into the reactor. Then, the mixture was heated in the silicon oil bath on a hot plate with continuous stirring to get required temperatures. The product was settled into three layers. The uppermost phase comprised of the solvent along with biodiesel was collected. Finally, evaporation was performed to remove excess solvent from the reaction mixture.

2.7. Catalyst regeneration

Reusability and regeneration tests were carried out by reutilizing the spent catalyst after every reaction. The mixture solvents (biodiesel and methanol) were removed from the reaction system from the microreactor, then the required amount of fresh crude lipid and methanol were put in to the microreactor. Lastly, the reaction was carried out under optimized conditions (MeOH:oil:catalyst wt.% (30:1:3) at 80 °C for 3 h). The above procedures were repeated until the significant drop on the FAME yield production.

2.8. FAME yield analysis

Gas chromatography (GC) (model 7890A, Agilent technologies) equipped with flame ionization detector (FID) was used to analyze the methyl ester yield. The silica capillary column (Agilent, HP-88 USA) with dimensions 300 m × 0.25 mm × 0.20 μm film thickness was used in this experiment. The helium was used as a carrier gas during the analysis. Methyl heptadecanoate and hexane were used as internal standard and solvent during the analysis of biodiesel. The chromatogram of biodiesel was shown in Supp. 1. The FAME yield was calculated according to EN 14103 procedures (Liu et al., 2006). An average value of triplicate measures was reported in all experiment.

2.9. Kinetic model

Transesterification of solid catalyst occurs at harsh reaction condition (higher temperature and pressure) has been reported. This phenomenon was due to the fact that three-phase catalytic reaction system slows down the transesterification reaction due to the mass transfer limitations (Arifin et al., 2009; Liu et al., 2006; Vyas et al., 2009; Rathore and Madras, 2007; Zhang et al., 2010). Stoichiometrically, reaction

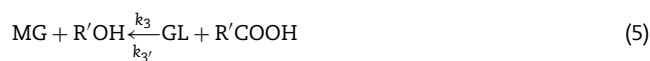
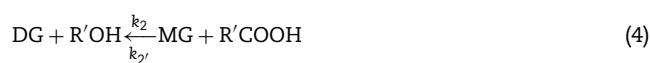
requires 3 mol of methanol (M) and 1 mol of triglyceride (TG) to give 3 mol of methyl ester (ME) and 1 mol of glycerol (GL), respectively, and the overall equation is shown as following Eq. (2).

In general, transesterification reaction comprises three consecutive reversible reactions (Eq. (3)), whereby 1 mol of ME is produced in each step and monoglycerides (MG) (Eq. (5)) and diglycerides (DG) (Eq. (4)) are intermediate product (Islam et al., 2013b).

Overall reaction



Stepwise reactions



Furthermore, the following assumption are used in this kinetic model i.e. (i) k_{eq} . must be not depending on methanol concentration and the reaction is considered pseudo-1st order), (ii) production of intermediate species is negligible and (iii) all chemical reaction only occurred in the oil phase. Therefore, first assumption (i) can be written as Eq. (6) as follows:

$$-r = \frac{d[\text{TG}]}{dt} = k[\text{TG}][\text{ROH}]^3 \quad (6)$$

Next, based on the second assumption (ii) (Eq. (8)),

$$k' = k[\text{ROH}]^3 \quad (7)$$

$$-r = \frac{d[\text{TG}]}{dt} = k[\text{TG}] \quad (8)$$

$$\ln \text{TG}_0 - \ln \text{TG} = k' \cdot t \quad (9)$$

And, according to the mass balance,

$$X_{\text{ME}} = 1 - \frac{[\text{TG}]}{[\text{TG}_0]} \quad (10)$$

$$[\text{TG}] = [\text{TG}_0][1 - X_{\text{ME}}] \quad (11)$$

$$\frac{dX_{\text{ME}}}{dt} = k'[1 - X_{\text{ME}}] \rightarrow -\ln(1 - X_{\text{ME}}) = k' \cdot t \quad (12)$$

Based on the equations above and experimental data, firstly, the concentration of ME at various reaction times (based on the moles fraction) was obtained. Secondly, a graph with $-\ln(1 - X_{\text{ME}})$ versus (T) was plotted using the Eq. (10) and the rate constant at each temperature were measured. Therefore, activation energy and pre-exponential factor was calculated by the Arrhenius equation (Eq. (13)):

$$k = A e^{-E_a/RT} \quad (13)$$

$$\ln k = \ln A - \frac{E_a}{RT} \quad (14)$$

where k is the reaction constant, A is the frequency or pre-exponential factor, E_a is the activation energy of the reaction,

Table 1 – Fatty acid content (a), moisture, free fatty acid and dried ash contents (b) of crude *N. oculata* microalgae based methyl esters.

(a)						
Substituent	Fatty acid	Common name	C	Molecular mass (g mol ⁻¹)	Composition in sample (%)	Molecular mass contribution (g mol ⁻¹)
Saturated lipid	Decanoic acid	Lauric acid	12:0	200.31	–	–
	Tetradecanoic acid	Myristic acid	14:0	228.37	7.69 ± 0.52	17.572
	Hexadecanoic acid	Palmitic acid	16:0	256.42	35.43 ± 0.06	90.862
	Octadecanoic acid	Stearic acid	18:0	284.48	2.50 ± 0.26	7.115
	Eicosanoic acid	Arachidic acid	20:0	312.54	–	–
Monounsaturated lipid	Hexadecenoic acid	Palmitoleic acid	16:1	254.41	27.54 ± 0.15	70.055
	cis-9-octadecenoic acid	Oleic acid	18:1	282.46	8.62 ± 0.02	24.335
	trans-9-octadecenoic acid	Elaidic acid	18:1	282.46	–	–
Polyunsaturated lipid	All cis-9,12-octadecadienoic acid	Linoleic acid	18:2	280.45	5.22 ± 0.23	14.643
	All cis-5,8,11,14-eicosatetraenic acid	Arachidonic acid	20:4	304.47	2.47 ± 0.05	7.529
	All cis-5,8,11,14,17-eicosatetraenic acid	EPA	20:5	302.45	8.29 ± 0.08	25.058
	All cis-4,7,10,13,16,19-docosahexenoic acid	DHA	22:6	328.49	2.24 ± 0.16	7.355
Average molecular weight of constituent fatty acid (AMW _{fatty acid})						264.525
Unsaturated/saturated lipid ratio						1.19
(b)						
Substituent						Content (%)
Moisture						5.47 ± 0.04
Free fatty acid						8.03 ± 0.31
Dried ash						10.68 ± 0.32

R is the gas constant and T is the absolute temperature. Plot of $\ln k$ versus $1/T$ are given from equation above (Eq. (14)), then E_a and pre-exponential factor have been calculated.

3. Results and discussion

3.1. Lipid characterization

The method reported by Bligh and Dyer was used to extract the highest lipid content from microalgae (*Nannochloropsis* sp.). As shown in Supp. 1 and Table 1, the fatty acid compositions of *Nannochloropsis* sp. contained mainly methyl esters of palmitic acid (35.43%), palmitoleic acid (27.54%), Oleic acid (8.62%), EPA (8.29%) and myristic acid (7.69%), respectively. Interestingly, the data exhibited that methyl ester of approximately 70% saturated fatty acid and 30% unsaturated fatty acid present in the biodiesel. The lower percentage of unsaturated fatty acids in algae biodiesel makes it more stable as compared to palm and tallow biodiesel (Sarin et al., 2007; Alcantara et al., 2000). Therefore, the calculated molecular weight (MW_{oil}) of microalgae oil was $831.62 \text{ g mol}^{-1}$ according to the following Eq. (15).

$$MW_{oil} = [(3 \times MW_{fatty\ acid}) + MW_{glycerol}] - 3 \times MW_{water} \quad (15)$$

Furthermore, the crude lipid also included a small fraction of moisture (5.47%), free fatty acid (8.03%) and dried ash (10.68%) (Table 1(b)).

3.2. Catalyst characterization

The TG-DTA profile of $\text{Ca}(\text{OCH}_3)_2$ catalyst under air flow environment is appeared in Fig. 1. The TGA curve remained constant with the temperatures ranging from 35 °C to 370 °C with minor weight loss indicating loss of moisture or volatile matters. The exothermic peak centered at 430 °C was attributed to the $\text{Ca}(\text{OCH}_3)_2$ decomposition reaction under oxygen condition to form calcium carbonate (Eq. (16)):

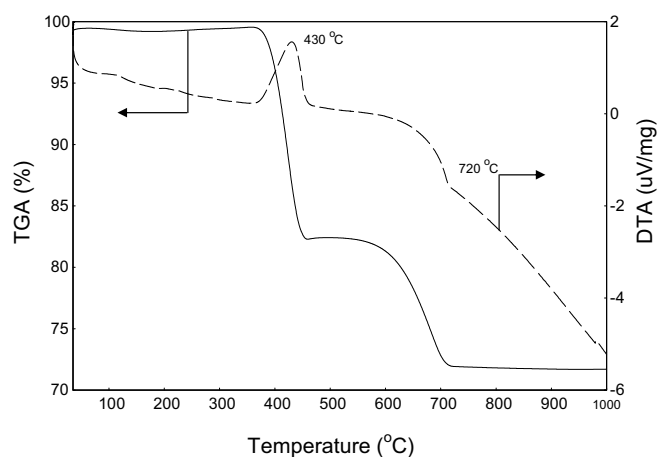


Fig. 1 – TG/DTA spectrum of $\text{Ca}(\text{OCH}_3)_2$ catalyst.

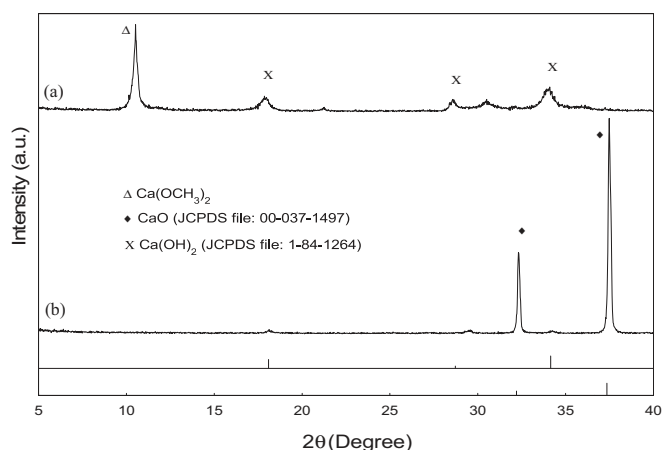


Fig. 2 – X-ray diffraction patterns of $\text{Ca}(\text{OCH}_3)_2$ (a) and CaO (b) catalysts. Δ , characteristic peak of $\text{Ca}(\text{OCH}_3)_2$; \blacklozenge , characteristic peak of CaO ; X , characteristic peak of $\text{Ca}(\text{OH})_2$.

Likewise, the second stage of weight loss was in the temperature range of 600–800 °C from the TGA curve indicating the thermal decomposition of calcium carbonate. At 720 °C, the transformation of CaCO_3 to stable CaO was caused, as confirmed from the DTA peak. The thermogravimetry analysis indicated that the synthesized $\text{Ca}(\text{OCH}_3)_2$ catalyst is stable up to 400 °C. A X-ray pattern of CaO and $\text{Ca}(\text{OCH}_3)_2$ catalysts is shown in Fig. 2. Two peaks at 2θ values of 32.1° and 37.2° (JCPDS File No. 00-037-1497) could be associated to the CaO phase. The main peaks at 2θ values of 10.8° was attributed to the $\text{Ca}(\text{OCH}_3)_2$ catalyst (Teo et al., 2015). In addition, three peaks at 2θ of 17.8°, 28.6° and 34.0° was corresponds to the existence of $\text{Ca}(\text{OH})_2$ (JCPDS file No: 01-84-1264) which could be formed due to the interaction of the catalyst with the water molecules.

The isotherms of catalyst, as shown in Fig. 3(a) resembles with Type IV according to the IUPAC classification with H3 type hysteresis loop (Sing et al., 1985). The surface area, average pore size and the pore volume of the catalyst (Fig. 3(b)) were $30 \text{ m}^2 \text{ g}^{-1}$, 32.97 nm and $0.21 \text{ cm}^3 \text{ g}^{-1}$, respectively (Table 2). The surface of $\text{Ca}(\text{OCH}_3)_2$ catalyst consist of mesopores ranging from 2 to 5 nm which could be related with the activity of catalyst in the transesterification reaction (Sing et al., 1985).

The FTIR spectrum of $\text{Ca}(\text{OCH}_3)_2$ catalyst (Fig. 5(a)) presented the important functional groups at 1070 cm^{-1} indicating C–O stretching vibration of primary alcohol. The stretching frequency peaks at 3650 cm^{-1} and $2800\text{--}3000 \text{ cm}^{-1}$ corresponding to the CH_3 and C–H stretching vibration of the catalyst, respectively, and are usually strong. Besides, peaks at 3650 cm^{-1} , could be due to the adsorption of moisture on the surface of the catalyst. Moreover, –OH groups were also existed as isolated substance on the surface of the catalyst (Ilgen and Akin, 2009). No organic functional group was observed on the CaO catalyst as shown in Fig. 4(b).

The irregular shape of CaO catalyst might be due to agglomeration of the bulk particles shown in (Fig. 5(a)). A flower-like cluster structure was observed in Fig. 5(b) which is similar to the result reported by Kouzu et al. (2008). A rapid mass

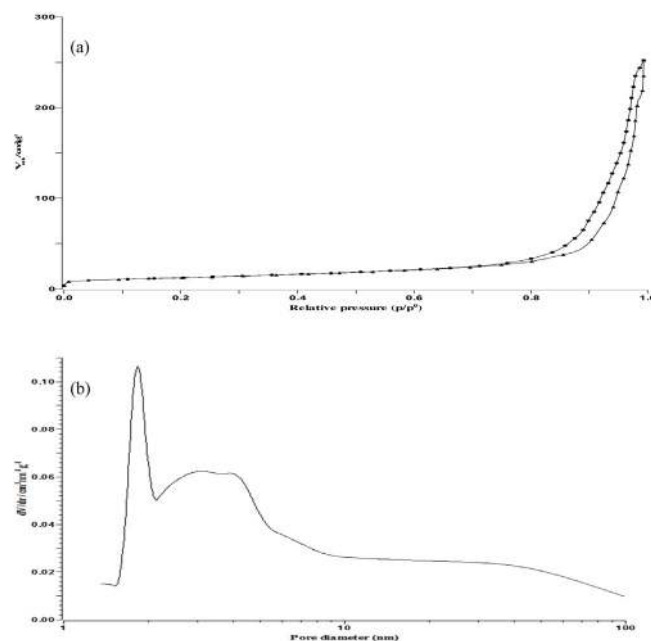


Fig. 3 – Nitrogen adsorption-desorption isotherms (a) and pore size distribution (b) of $\text{Ca}(\text{OCH}_3)_2$ catalyst.

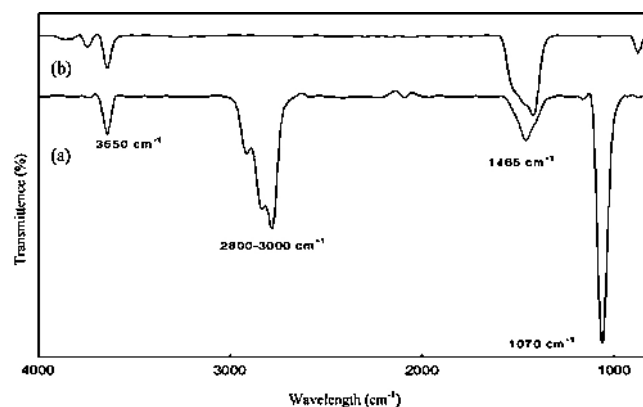


Fig. 4 – FTIR spectra of $\text{Ca}(\text{OCH}_3)_2$ (a) and CaO (b) catalysts.

transfer into the interstices of the catalyst could be provided by flower-like cluster structure as reported by Kouzu et al. (2008). TEM images of CaO (Fig. 5(c)) and $\text{Ca}(\text{OCH}_3)_2$ (Fig. 5(d)) catalysts revealed to be cubic in shape. Both images are consistent with result obtained from FESEM study, as shown in Fig. 5(a) and (b).

3.3. Process optimization of transesterification

The molar ratio of methanol to algae oil was varied from 10:1 to 60:1, as can be seen in Fig. 6. The FAME yield derived from crude microalgae lipid was increased significantly from 6.9% to 85.4% with methanol molar ratio of 10:1–60:1. As reported by several researchers (Islam et al., 2013a,b) that high amount of methanol could be accelerated the transesterification reaction rate. Fig. 7 demonstrated the effect of the $\text{Ca}(\text{OCH}_3)_2$ catalyst dosage on biodiesel yield. The concentration of catalyst

Table 2 – BET surface area, total pore volume and average pore diameter of $\text{Ca}(\text{OCH}_3)_2$ and CaO catalysts.

Catalyst	a_{BET} ($\text{m}^2 \text{ g}^{-1}$)	Total pore volume ($\text{cm}^3 \text{ g}^{-1}$)	Average pore diameter (nm)
$\text{Ca}(\text{OCH}_3)_2$	30.5	0.21	31.97
CaO	6.3	0.04	3.12

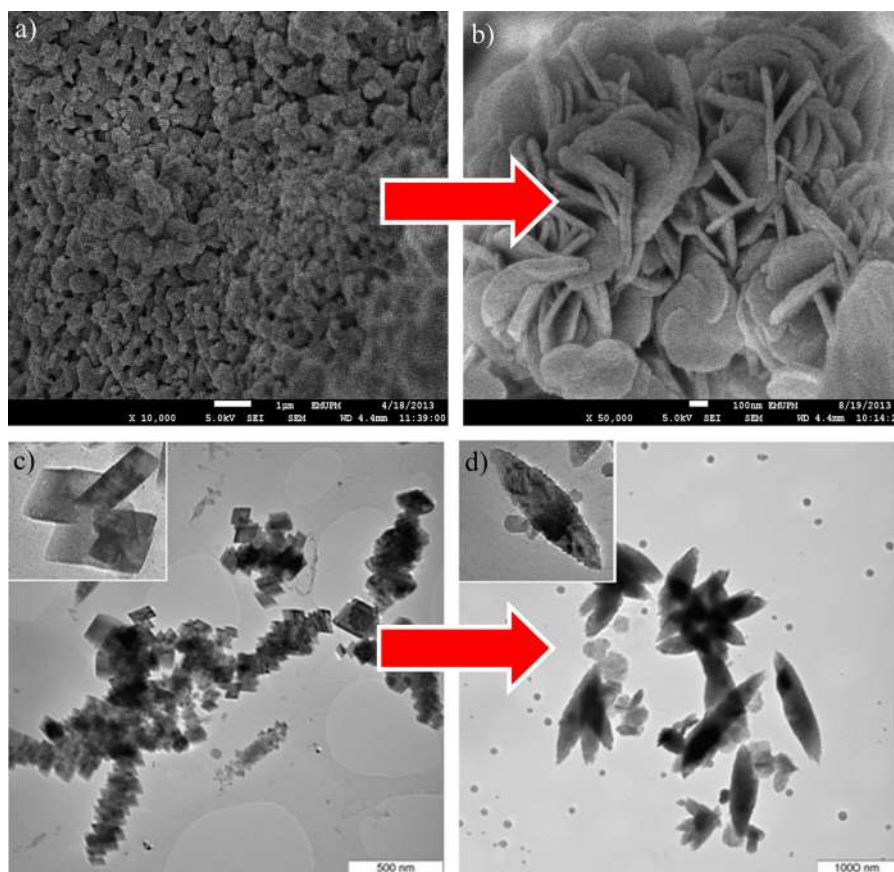


Fig. 5 – SEM (a and b) and TEM (c and d) micrographs of CaO and Ga(OCH₃)₂ catalysts.

during the reaction was varied from 0 to 15 wt.% for 3 h at 60 °C. The maximum FAME yield of 92.0% was obtained at 12 wt.% of catalyst dosage. However, the yield was started to drop to 61.6% with further increasing the catalyst loading to 15 wt.%. This could be attributed to the poor diffusion between the methanol–oil–catalyst systems when catalyst overloading in the reaction system. The high activity of the catalyst could be due to the formation of active CH₃O[−] species dissociated for methanol attached to the triglyceride molecule under the optimum catalyst concentrations (Islam et al., 2013a,b).

As can be seen that the triglyceride (TG) was converted into biodiesel by 20–30 min of reaction time (Fig. 8). The results indicated that the reaction rate obtained from the homogeneous NaOH catalyst was significantly faster reaction

compared the heterogeneous catalysts. On the other hand, the reaction rate of heterogeneous catalyst system (Ca(OCH₃)₂ and CaO) is very slow and it achieved high FAME yield after the reaction time of 3 h. However, the conversion rate of 92% FAME yield was observed for Ca(OCH₃)₂ catalyst compared to conversion 80% over the CaO after the same duration. In this case, homogeneous system (NaOH) shows fast conversion rate and reach maximum yield at a short reaction time, however, the formation of other intermediates and saponification are the main drawbacks of the liquid catalyst (Nautiyal et al., 2014). The influence of reaction temperature is very important for heterogeneously catalyzed. This is because high reaction temperature requires more energy use in the process. Fig. 9 present the variation of temperature on crude microalgae oil transesterification was studied at 3 wt.% catalyst loading and

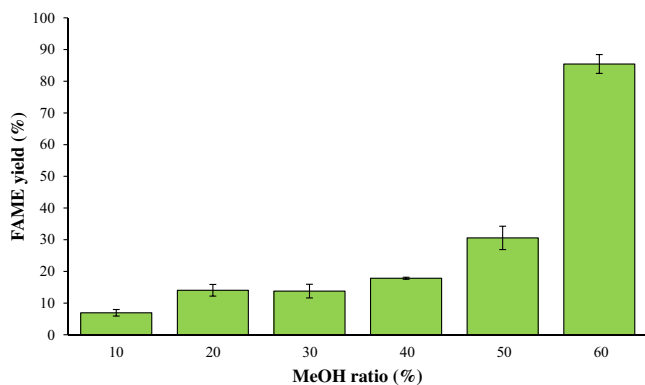


Fig. 6 – Influence of methanol/oil molar ratio on the FAME yield of crude microalgae lipid by Ca(OCH₃)₂ catalyst. Reaction condition: catalyst dosage = 3 wt.%, reaction time = 3 h, reaction temperature = 60 °C.

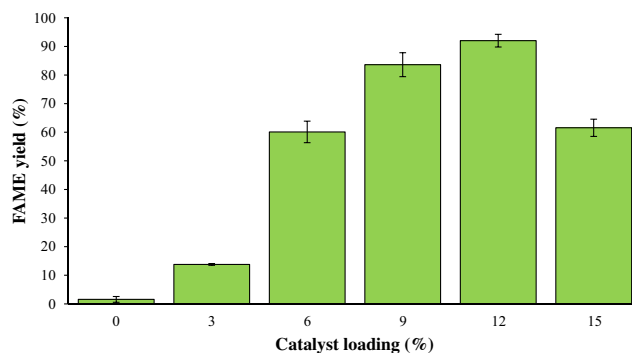


Fig. 7 – Influence of Ca(OCH₃)₂ catalyst loading on the FAME yield of crude microalgae lipid by Ca(OCH₃)₂ catalyst. Reaction condition: n(methanol):n(lipid) = 30:1, reaction time = 3 h, reaction temperature = 60 °C.

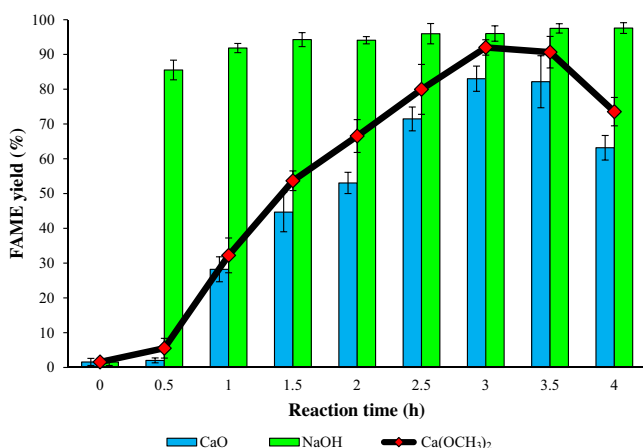


Fig. 8 – Influence of reaction time on the FAME yield of crude microalgae lipid by $\text{Ca}(\text{OCH}_3)_2$ (a), CaO (b) and NaOH (c) catalyst. Reaction condition: catalyst dosage = 12 wt.% (a and b) and 1 mol (c), $n(\text{methanol}):n(\text{oil}) = 30:1$, reaction temperature = 60 °C.

methanol/oil molar ratio of 30:1. The reaction was performed at four different temperatures of 50, 60, 70 and 80 °C. As can be seen from Fig. 9 that the yield was reached to 52% at 50 °C after 180 min of reaction time whereas the yield increased to 92%, 97% and 99% at 60, 70 and 80 °C, respectively after the same reaction time. Transesterification of oil with methanol in the presence of heterogeneous catalyst is a three-phase reaction system. Therefore, raising the reaction temperature favored the transesterification due to the enhancement of miscibility at high temperature.

3.4. Kinetic of transesterification

Depending on the systems, pseudo-second-order (Birla et al., 2012), reversible second-order (Hassan and Vinjamur, 2014), or pseudo-first-order (Nautiyal et al., 2014), kinetic models have been reported for biodiesel production. In most cases, pseudo-first-order kinetics has been observed in the presence of excess methanol (Sivasamy et al., 2009). As can be seen from Fig. 10, the fitted straight lines are not passing through origin for the initial reaction kinetics, which means that the reaction obeys irreversible second-order kinetic during the initial period (Hassan and Vinjamur, 2014). This irreversible kinetics in the initial period is in agreement with sulfuric

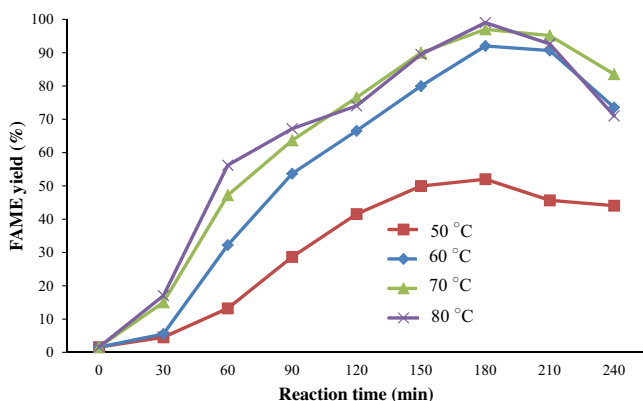


Fig. 9 – Influence of reaction temperature on the FAME yield of crude microalgae lipid by $\text{Ca}(\text{OCH}_3)_2$ catalyst. Reaction condition: $n(\text{methanol}):n(\text{lipid}) = 30:1$, reaction time = 0.5–4 h, catalyst loading = 3 wt.%.

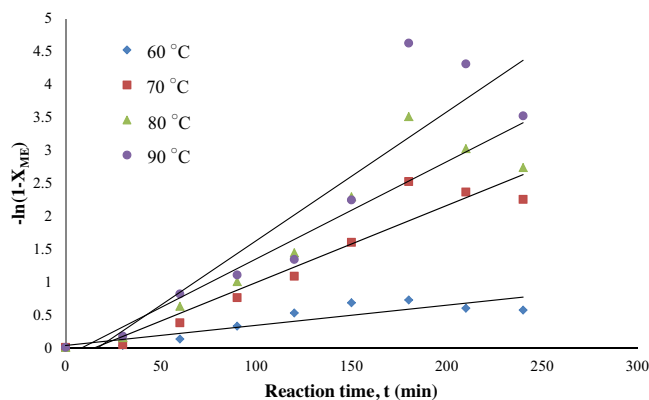


Fig. 10 – Arrhenius plot $\ln k$ versus $1/T \times 10^3$ for transesterification reaction in the presence of $\text{Ca}(\text{OCH}_3)_2$ catalyst. Reaction condition: $n(\text{methanol}):n(\text{lipid}) = 30:1$, reaction time = 0.5–4 h, catalyst loading = 3 wt.%.

acid-catalyzed esterification of fatty acids with methanol reported by Boucher et al. (2008). A similar conclusion has been reached by Liu et al. (2006) by comparing both the activity-based and concentration-based approaches in their studies.

The values of rate constant calculated from Eq. (13) for both regimes obtained at reaction temperatures of 50, 60, 70 and 80 °C, which are 0.003, 0.011, 0.014 and 0.019 min^{-1} , respectively. It has been shown by the researchers that the rate constant varies by the reaction parameter i.e. fatty acid composition oil and process used for transesterification. The values of reaction rate constant from *Spirulina platensis* algae biomass were reported to be 0.001 min^{-1} under optimized operating conditions (Nautiyal et al., 2014). Vyas et al. (2009) reported the rate constant values varied from 0.0031 to 0.0363 min^{-1} for biodiesel production through transesterification of *Jatropha* oil at temperatures ranges from 50 to 70 °C. The rate constant of the transesterification reaction varies from 0.001 to 0.006 min^{-1} , as reported by several researchers (Rathore and Madras, 2007). Some authors (Kaur and Ali, 2014a) reported the higher rate constant (0.03 min^{-1}) for the ethanolysis of waste cottonseed oil over lithium impregnated calcium oxide. Thus, the value of rate constant obtained in this study was consistent with the values reported in the literature.

Furthermore, the Arrhenius energy of activation from a plot of the reaction rate constant (k) versus the reciprocal of absolute temperature (T) was determined from values of rate constants at different temperatures (Fig. 11). The slope and

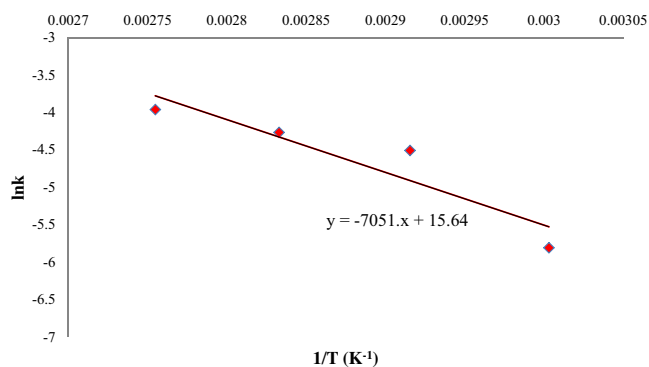


Fig. 11 – $\ln(1 - X_A)$ versus time plot for transesterification reaction in the presence of $\text{Ca}(\text{OCH}_3)_2$ catalyst. Reaction condition: $n(\text{methanol}):n(\text{lipid}) = 30:1$, reaction time = 0.5–4 h, catalyst loading = 3 wt.%.

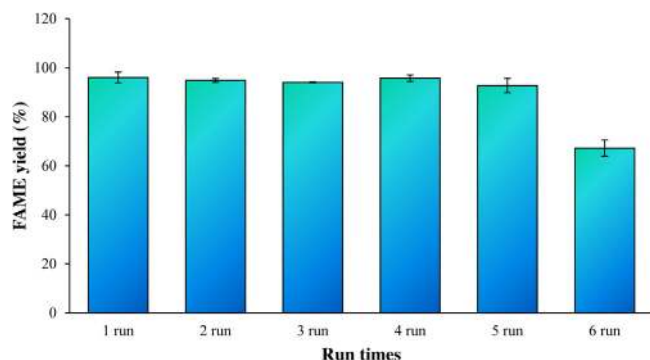


Fig. 12 – Stability and reusability test.

intercept of the graph between $\ln k$ versus $1/T \times 10^3$ gives the values of activation energy and frequency factor. The observed E_a value in present study ($58.62 \text{ kJ mol}^{-1}$) was found within the range of reported values ($41\text{--}66 \text{ kJ mol}^{-1}$) for transesterification reaction catalyzed by heterogeneous catalysts (Kaur and Ali, 2014b,c, 2015). Zhang et al. (2010) reported higher activation energy for the transesterification catalyzed of waste frying oil using potassium hydroxide (79.1 kJ mol^{-1}) and snail shell derived catalysts (79 kJ mol^{-1}), respectively. This implies that, on increasing the temperature, the side reactions leading to soap formation are more favored than the ones producing biodiesel (Eze et al., 2014).

A conclusion has been reached by Nautiyal et al. (2014) that the higher amount of unsaturated fatty acid (52% of linoleic

acid) presence in the waste cooking oil may increase the value activation energy. Further, it has been shown by other workers (Lee et al., 2010) that the activation energy for particular reactions is influenced by the concentration of catalyst, reaction temperature, nature of reactant, etc. Thus, the reason for the lower value of activation energy as compared to values obtained for waste frying oil could be due to the catalyst used in this study.

3.5. Durability of catalyst

In order to evaluate the catalyst sustainable, the used $\text{Ca}(\text{OCH}_3)_2$ catalyst was washed thoroughly with methanol and hexane, then, dried in an oven for overnight after each experiment (Fig. 12). The catalyst was reused for transesterifying operation up to 5 times and sustained the activity to produce FAME yield at range of 92.7–96.0%. However, the yield of FAME was reduced to 67.2%. After 5th runs of transesterification reaction, the well defined flower-like cluster crystallites structure of $\text{Ca}(\text{OCH}_3)_2$ catalyst (Fig. 5(b)) was reorganized in aggregates in a cakes-like sticky structure of $\text{Ca}(\text{OH})_2$ (Fig. 13(a)). This rephrase in the catalyst bulk morphology led to a deactivation of the catalyst by blocking the contact between the active catalytic sites and the reactants. These results are consistent with the obtained XRD profile on the existing $\text{Ca}(\text{OH})_2$ crystal phases (Fig. 13(b)). A conclusion has been also reached by Teo et al. (2015) that the catalyst might be deactivated by the impurities e.g., phospholipids and moisture presence in the reaction medium.

4. Conclusions

The present study showed that nano $\text{Ca}(\text{OCH}_3)_2$ catalyst is an effective solid catalyst for biodiesel production from *Nannochloropsis* microalgae. It is inexpensive and environment friendly, has high catalytic activity. The high activity of the catalyst was described to the methoxide species (CH_3O^-) that allowed more methanol to contact with the carbonyl group of triglyceride. The high specific surface area and large pore size are favorable for contact between catalyst and substrates, which effectively improved efficiency of transesterification. The maximum conversion was achieved as 99.0% at 80°C , 30:1 molar ratio of methanol to oil and 3 wt.% of catalyst. This result indicates that the new route of synthesis has provided a sustainable way with significant benefits for an environmentally benign procedure in produce biodiesel.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.cherd.2016.04.012](https://doi.org/10.1016/j.cherd.2016.04.012).

References

- Alcantara, R., Amores, J., Canoira, L.T., Fidalgo, E., Franco, M.J., Navarro, A., 2000. Catalytic production of biodiesel from soy-bean oil used frying oil and tallow. *Biomass Bioenergy* 18 (6), 515–527.
- Andrikopoulos, N.K., Giannakis, I.G., Tzamtzis, V., 2001. Analysis of olive oil and seed oil triglycerides by capillary gas chromatography as a tool for the detection of the adulteration of olive oil. *J. Chromatogr. Sci.* 39, 137–145.
- Arifin, A.A., Bakar, J., Tan, C.P., Rahman, R.A., Krim, R., Loi, C.C., 2009. Differential scanning calorimetric analysis of edible oils:

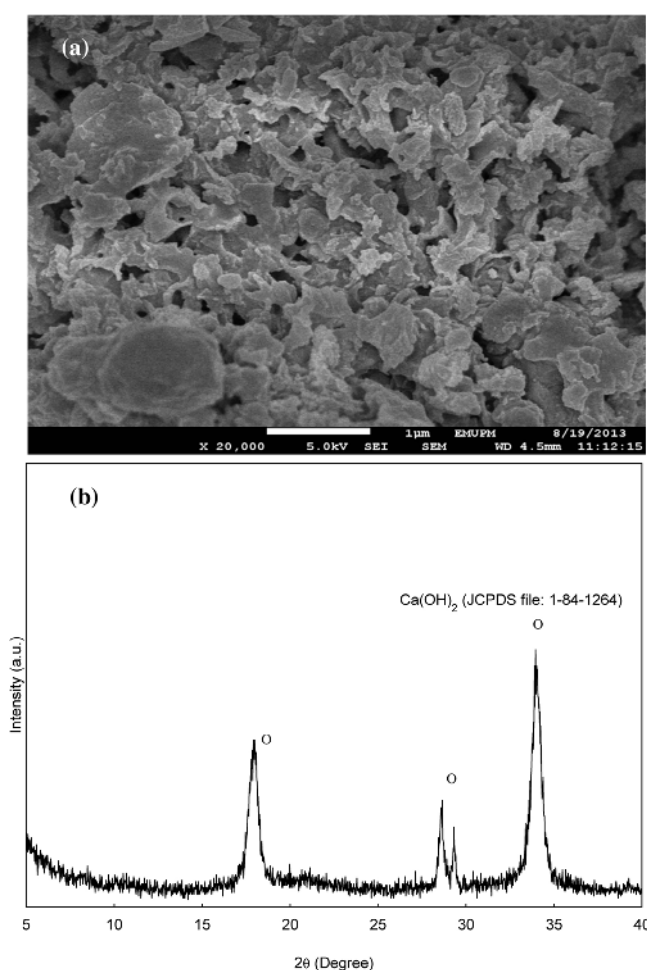


Fig. 13 – SEM micrograph (a) and XRD pattern (b) of deactivated $\text{Ca}(\text{OCH}_3)_2$ catalyst.

- comparison of thermal properties and chemical composition. *Food Chem.* 114, 561–564.
- Asakuma, Y., Maeda, K., Kuramochi, H., Fukui, K., 2009. Theoretical study of the transesterification of triglycerides to biodiesel fuel. *Fuel* 88 (5), 786–791.
- Birla, A., Singh, B., Upadhyay, S.N., Sharma, Y.C., 2012. Kinetics studies of synthesis of biodiesel from waste frying oil using a heterogeneous catalyst derived from snail. *Bioresour. Technol.* 106, 95–100.
- Boucher, M.B., Unker, S.A., Hawley, K.R., Wilhite, B.A., Stuart, J.D., Parnas, R.S., 2008. Variables affecting homogeneous acid catalyst recoverability and reuse after esterification of concentrated omega-9 polyunsaturated fatty acids in vegetable oil triglycerides. *Green Chem.* 10, 1331–1336.
- Eze, V.C., Phan, A.N., Harvey, A.P., 2014. A more robust model of the biodiesel reaction, allowing identification of process conditions for significantly enhanced rate and water tolerance. *Bioresour. Technol.* 156, 222–231.
- Hassan, S.Z., Vinjamur, M., 2014. Concentration-independent rate constant for biodiesel synthesis from homogeneous-catalytic esterification of free fatty acid. *Chem. Eng. Sci.* 107, 290–301.
- Ilgel, O., Akin, A.N., 2009. Transesterification of canola oil to biodiesel using MgO loaded with KOH as a heterogeneous catalyst. *Energy Fuels* 23, 1786–1789.
- Islam, A., Taufiq-Yap, Y.H., Chu, C.M., Ravindra, P., Chan, E.S., 2013a. Transesterification of palm oil using KF and NaNO₃ catalysts supported on spherical millimetric γ -Al₂O₃. *Renew. Energy* 59, 23–29.
- Islam, A., Taufiq-Yap, Y.H., Chu, C.M., Chan, E.S., Ravindra, P., 2013b. Studies on design of heterogeneous catalysts for biodiesel production. *Process Saf. Environ.* 91, 131–144.
- Islam, A., Chan, E.S., Taufiq-Yap, Y.H., Mondal, M.A.H., Moniruzzaman, M., Mridha, M., 2014. Energy security in Bangladesh perspective—an assessment and implication. *Renew. Sustain. Energy Rev.* 32, 154–171.
- Kaur, M., Ali, A., 2014a. Potassium fluoride impregnated CaO/NiO: an efficient heterogeneous catalyst for transesterification of waste cottonseed oil. *Eur. J. Lipid Sci. Technol.* 116 (1), 80–88.
- Kaur, N., Ali, A., 2014b. Kinetics and reusability of Zr/CaO as heterogeneous catalyst for the ethanolysis and methanolysis of *Jatropha crucas* oil. *Fuel Process. Technol.* 119, 173–184.
- Kaur, M., Ali, A., 2014c. Ethanolysis of waste cottonseed oil over lithium impregnated calcium oxide: kinetics and reusability studies. *Renew. Energy* 63, 272–279.
- Kaur, N., Ali, A., 2015. Biodiesel production via ethanolysis of jatropha oil using molybdenum impregnated calcium oxide as solid catalyst. *RSC Adv.* 5 (18), 13285–13295.
- Kouzu, M., Kasuno, T., Tajika, M., Yamanaka, S., Hidaka, J., 2008. Active phase of calcium oxide used as solid base catalyst for transesterification of soybean oil with refluxing methanol. *Appl. Catal. A: Gen.* 334, 357–365.
- Lam, M.K., Lee, K.T., 2012. Potential of using organic fertilizer to cultivate *Chlorella vulgaris* for biodiesel production. *Appl. Energy* 94, 303–308.
- Lam, M.K., Lee, K.T., Mohamad, A.R., 2012. Microalgae biofuels: a critical review of issues, problems and the way forward. *Biotechnol. Adv.* 30 (3), 673–690.
- Lee, J.Y., Yoo, C., Jun, S.Y., Ahn, C.Y., Oh, H.M., 2010. Comparison of several methods for effective lipid extraction from microalgae. *Bioresour. Technol.* 101, 75–77.
- Liu, Y., Lotero, E., Goodwin Jr., J.G., 2006. Effect of water on sulfuric acid catalyzed esterification. *J. Mol. Catal. A: Chem.* 245, 132–140.
- Nautiyal, P., Subramanian, K.A., Dastidar, M.G., 2014. Kinetic and thermodynamic studies on biodiesel production from *Spirulina platensis* algae biomass using single stage extraction–transesterification process. *Fuel* 135, 228–234.
- Palligarnai, T.V., Michael, B., 2008. Biodiesel production—current state of the art and challenges. *J. Indian Microbiol. Biotechnol.* 35, 421–430.
- Rathore, V., Madras, G., 2007. Synthesis of biodiesel from edible and non-edible oils in supercritical alcohols and enzymatic synthesis in supercritical carbon dioxide. *Fuel* 86 (17), 2650–2659.
- Sarin, R., Sharma, M., Sinharay, S., Malhotra, R.K., 2007. *Jatropha*-palm biodiesel blends: an optimum mix for Asia. *Fuel* 86 (10), 1365–1371.
- Shahbazi, M.R., Khoshandam, B., Nasiri, M., Ghazvini, M., 2012. Biodiesel production via alkali-catalyzed transesterification of Malaysian RBD palm oil – characterization, kinetics model. *J. Taiwan Inst. Chem. Eng.* 43 (4), 504–510.
- Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscou, L., Pierotti, R.A., Rouquerol, J., 1985. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure Appl. Chem.* 57, 603–619.
- Sivasamy, A., Cheah, K.Y., Fornasiero, P., Kemausuor, F., Zinoviev, S., Miertus, S., 2009. Catalytic applications in the production of biodiesel from vegetable oils. *ChemSusChem* 2 (4), 278–300.
- Teo, S.H., Islam, A., Ng, F.L., Taufiq-Yap, Y.H., 2015. Biodiesel synthesis from photoautotrophic cultivated oleaginous microalgae using a sand dollar catalyst. *RSC Adv.* 5 (6), 4266–4276.
- Uzun, B.B., Kılıç, M., Özbay, N., Pütün, A.E., Pütün, E., 2012. Biodiesel production from waste frying oils: optimization of reaction parameters and determination of fuel properties. *Energy* 44 (1), 347–351.
- Vyas, A.P., Subrahmanyam, N., Patel, P.A., 2009. Production of biodiesel through transesterification of *Jatropha* oil using KNO₃/Al₂O₃ solid catalyst. *Fuel* 88 (4), 625–628.
- Xie, W.L., Fan, M.L., 2014. Biodiesel production by transesterification using tetraalkylammonium hydroxides immobilized onto SBA-15 as a solid catalyst. *Chem. Eng. J.* 239, 60–67.
- Xie, W., Zhao, L.L., 2013. Production of biodiesel by transesterification of soybean oil using calcium supported tin oxides as heterogeneous catalysts. *Energy Convers. Manag.* 76, 55–62.
- Xie, W.L., Zhao, L.L., 2014. Heterogeneous CaO–MoO₃–SBA-15 catalysts for biodiesel production from soybean oil. *Energy Convers. Manag.* 79, 34–42.
- Xie, W., Wang, H., Li, H., 2011. Silica-supported tin oxides as heterogeneous acid catalysts for transesterification of soybean oil with methanol. *Ind. Eng. Chem. Res.* 51 (1), 225–231.
- Zhang, L., Sheng, B., Xin, Z., Liu, Q., Sun, S., 2010. Kinetics of transesterification of palm oil and dimethyl carbonate for biodiesel production at the catalysis of heterogeneous base catalyst. *Bioresour. Technol.* 101, 8144–8150.