Chemical Engineering Journal 165 (2010) 798–805

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Transesterification of soybean oil catalyzed by fly ash and egg shell derived solid catalysts

R. Chakraborty*, S. Bepari, A. Banerjee

Department of Chemical Engineering, Jadavpur University, 188 Raja S.C. Mullik Road, Kolkata 700032, India

ARTICLE INFO

Article history:
Received 31 May 2010
Received in revised form 5 October 2010
Accepted 8 October 2010

Keywords:
Transesterification
Soybean oil
Fly ash supported heterogeneous catalyst
Biodiesel
Waste egg shell
RSM optimization

ABSTRACT

A fly ash supported heterogeneous CaO catalyst has been developed using waste egg shell for transesterification of soybean oil to yield fuel grade biodiesel. The active metal precursor $Ca(OH)_2$ of the catalyst has been economically derived from waste egg shell calcination and the mesoporous, high activity strong base catalyst has been prepared using wet-impregnation method. X-ray diffraction (XRD), scanning electron microscope (SEM), low temperature N_2 adsorption–desorption (BET) and BJH method studies manifested the well-dispersed presence of CaO over the fly ash framework. The specific surface area of 0.701 m^2/g, pore volume of 0.0044 cm^3/g, 5.2 nm pore diameter and 1.6 mmol HCl/g catalyst basicity rendered high catalyst activity which could be demonstrated through high biodiesel yield from refined soybean oil by transesterification with methanol. A three factor–three level face centered central composite design (FCCD) has been used to evaluate the effects of process parameters on yield of fatty acid methyl ester (FAME). Optimal parametric values computed using response surface methodology (RSM) corresponding to maximum (i.e. 96.97%) FAME yield were CaO loading of 30 wt.%, 1.0 wt.% catalyst concentration and 6.9:1 methanol/oil molar ratio. The developed catalyst exhibited higher reusability characteristic and superior catalytic activity compared to unsupported CaO catalyst derived from egg shell. An effective waste valorization avenue could, thus, be procreated through preparation of a novel low cost heterogeneous catalyst from these industrial and municipal wastes for synthesis of fuel grade biodiesel.

1. Introduction

The ever increasing world population coupled with rise in petroleum price and environmental problems have necessitated the finding of environmentally benign and renewable energy. Biodiesel is a diesel type fuel composed of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, demonstrating several advantages as being biodegradable, renewable, nontoxic fuel. It is thus helping to achieve the EU renewable energy target (12% of total energy output to consist of renewable energy by 2010) [1]. The biodiesel production is commonly performed by transesterification of refined vegetable oils with methanol in the presence of homogeneous base catalysts, such as sodium or potassium hydroxides, carbonates or alkoxides. But these catalysts have some problems such as difficulty in removing the catalysts after the reaction, production of large amount of wastewater and emulsification [2].

In order to overcome the drawbacks of homogeneous catalytic process, recently profound attention has been devoted to the development and application of heterogeneous catalysts for synthesis of biodiesel. Several attempts were made [3–5] to prepare solid acid catalysts for transesterification. Solid acid catalyst comprising of $SO_4{}^{2-}/TiO_2–SiO_2$ was exhibited as capable of performing esterification and transesterification simultaneously to synthesize biodiesel from several low cost feedstocks with high FFAs [6]. However, the acceptable catalytic activity was achieved at the expense of high reaction temperature (200 °C). Similarly, investigations have been reported on heterogeneous base catalysts viz. unsupported CaO, $Sr(NO_3)_2/ZnO$, KI/Al_2O_3, $Na/NaOH/Al_2O_3$, KF/MgO, ion-exchange resins etc. capable of conducting transesterification reaction [7–12]. In all cases direct utilization of analytical reagent grade chemicals have been attempted [13,14] for catalyst preparation invoking high cost. Successful ventures were reported on utilization of wastes viz. chicken egg shell [15], oyster shell [16], mud crab shell [17] and mollusk shell [18] as cheap resources of CaO for application as low cost heterogeneous catalyst for biodiesel synthesis; although, no attempt has been reported to develop supported-CaO catalyst from these waste resources for obtaining a superior catalyst in terms of reusability and higher catalytic activity. However, a few research works [19–22] have been published on development and application of Al_2O_3/SiO_2 supported CaO catalysts from reagent grade chemicals for synthesis of biodiesel.

---

* Corresponding author. Tel.: +91 3324146378; fax: +91 3324146378.
E-mail address: rajat_chakraborty25@yahoo.com (R. Chakraborty).

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.10.019

Fly ash, the chief inorganic waste arises through coal combustion processes at coal-based thermal power plants, has a typical chemical composition (on dry basis): 55.19% SiO_2, 30.01% Al_2O_3, 4.58% Fe_2O_3, 2.12% Na_2O, 0.77% CaO, 1.91% MgO, 2.74% TiO_2, 1.28% BaO and 1.40% K_2O [23]. The presence of high amount of SiO_2 and Al_2O_3 prompts its potential applicability as a low-cost catalyst support. In a very recent publication, fly ash supported calcium oxide has been employed as a recyclable solid base catalyst for Knoevenagel condensation reaction [24]; however, the CaO was derived from reagent grade $CaCO_3$ which might increase the cost of catalyst preparation.

Thus, the present work attempts to develop and characterize a novel low cost, highly efficient supported base catalyst through utilization of the two waste materials viz. fly ash and egg shell for transesterification of refined soybean oil (SO) to yield fuel grade biodiesel. The effects of various process parameters viz. wt.% CaO loading, alcohol to oil molar ratio and catalyst concentration on the yield of fatty acid methyl ester (FAME) were investigated through a face centered central composite design (FCCD) and the optimal process conditions corresponding to maximum FAME yield have been determined using response surface methodology (RSM).

2. Experimental

2.1. Materials

Refined soybean oil was procured from local market. Chicken egg shell was collected from local restaurants. Fly ash was collected from Kolaghat Thermal Power Plant, West Bengal, India. As this fly ash [23] contains at least 70% ($SiO_2 + Al_2O_3 + Fe_2O_3$), thus, it can be categorized as class F fly ash as per ASTM C618. All the chemicals used were of reagent grade. Methanol (>99% purity), anhydrous sodium sulphate (Na_2SO_4), acetone, etc. were purchased from Merck.

2.2. Catalyst preparation

The waste egg shells were washed with distilled water thrice to remove impurities and subsequently treated in hot air oven at 105 °C for about 24 h for removal of adhering water. The dried shells were ground to fine powder and calcined in a muffle furnace at 1000 °C for 2 h [15] to generate CaO in order to subsequently obtain the active salt precursor i.e. $Ca(OH)_2$. The fly ash was wet ground for 16 h using a ball mill followed by drying in hot air oven at 100 ± 5 °C for 24 h. The fly ash supported CaO catalyst was prepared following wet impregnation method [25]. Typically, in order to prepare 10 wt.% CaO loaded catalyst, 3 g of calcined egg shell powder was added to 200 ml of water to prepare aqueous solution of $Ca(OH)_2$; this solution was subsequently added to 27 g of pre-dried fly ash and mixed vigorously using mechanical agitator under total reflux for 4 h, at 70 °C and pH of 12.10. The solution was aged for 24 h for formation of the $Ca(OH)_2$ precipitate on fly ash carrier. Excess water was removed using hot air oven at 100 °C for 20 h. The dried mass was finally calcined in muffle furnace at temperature of 1000 °C for 2 h to prepare the fly ash supported base catalyst.

2.3. Catalyst characterization

In order to determine the crystalline nature of fly ash supported CaO catalysts, X-ray diffraction (XRD) patterns for each (10–30 wt.% CaO loading) supported catalyst samples were analyzed using Cu-Kα source equipped with an Inel CPS 120 hemispherical detector (Rigaku Miniflex Co., Japan). The analysis was performed at 2θ angle ranging from 20° to 80° at a scanning speed of $1^\circ\ \text{min}^{-1}$. The surface morphology of the developed catalyst was determined using scanning electron microscope (SEM) at 15 kV (JEOL Ltd, Japan, JSM-5200). The specific surface area of the fly ash supported catalyst sample was measured by BET method using low temperature N_2 adsorption–desorption (Quantachrome Autosorb 1C). The sample was tested for pore volume and pore size distribution using BJH (Barret, Joyner and Halenda) method.

In our study, the method of titration was used to determine the basicity of the catalysts as per the literature [26] reported method. In a typical test, 1 g of the catalyst was mixed and reacted with 50 ml of 1 N hydrochloric acid at 30 °C. The basic catalyst could neutralize HCl by an equivalent amount to its basicity. Consequently, the original concentration of HCl was reduced. The final concentration of HCl was determined by titration (neutralization) with 1 N NaOH using phenolphthalein indicator; the adsorbed amount of HCl on the catalyst could, thus, be determined.

2.4. Equipment

The experimental batch reactor comprised of a three necked 1 L capacity borosil flask which was heated using a heating mantle provided with a PID temperature controller to maintain isothermal condition corresponding to the set point for biodiesel synthesis from refined soybean oil using fly ash supported CaO catalyst. The two necks of the flask were fitted with two reflux condensers to maintain constant molar ratio of methanol to oil over the entire span of transesterification reaction. The reaction mixture was agitated by a centrally placed motorized stirrer equipped with a digital speed regulator.

2.5. Transesterification reaction procedure

Methanolysis of refined soybean oil was initiated in the batch reactor (described in Section 2.4) by charging fixed quantity of refined soybean oil (89.8 g, 100 mL) and measured amount of catalyst (1.0–5.0 wt.% of oil). The mixture was then stirred for few minutes to make uniformly mixed oil-catalyst slurry and heated to 70 °C [27], followed by addition of methanol. Our preliminary study revealed that, for methanol/oil molar ratio below 5.5, insignificant amount of FAME yields were obtained. Noureddini and Zhu [28] and Jitputti et al. [4] reported 6:1 methanol to oil molar ratio for synthesis of biodiesel; while, Singh and Fernando [26] used 7:1 methanol to soybean oil molar ratio for transesterification of soybean oil using heterogeneous catalysts. Thus, in the present study, the alcohol/oil molar ratio was varied from 5.5 to 6.9 which were very close to that (from 5:1 to 7:1) reported by Bouaid et al. [29] in RSM optimization study for biodiesel synthesis. Besides, as the methanol used in the present study contains about 1% impurity containing water; higher methanol to oil ratio might lead to some extent of catalyst deactivation due to formation of $Ca(OH)_2$ (Section 3.5). After carrying out the reaction for 5 h [16] at a regulated stirrer speed of 500 rpm [13,17], the reaction mixture was equilibrated to room temperature and transferred to a laboratory scale vacuum filter for solid catalyst separation. After filtration, the filtrate was centrifuged at about 4000 rpm for 0.25 h for separation of the ester phase from glycerol phase. Biodiesel was obtained as the top layer while glycerol at the bottom; the top layer was then purified through distillation in a laboratory scale batch vacuum distillation unit to recover unreacted methanol. The traces of methanol from biodiesel layer were removed by washing with hot distilled water for thrice followed by drying with anhydrous Na_2SO_4 in order to conform to the ASTM D6751.

2.6. Yield, purity and fuel properties of synthesized biodiesel

The yield of fatty acid methyl ester (FAME) obtained through transesterification of soybean oil was calculated using an equation

Table 1
Experimental ranges and levels of the independent variables for response surface study.

Factors	Name	Units	−1 level	0 level	+1 level
X_L	CaO loading	wt.%	10.00	20.00	30.00
X_C	Catalyst concentration	wt.% of oil	1.00	3.00	5.00
X_{MR}	Methanol/oil molar ratio	–	5.50	6.20	6.90

similar to [30]:

$$Y_{FAME} = \left(\frac{W_b}{W_o}\right) p_{FAME} \tag{1}$$

In our study, the quantitative FAME content of biodiesel was determined by gas chromatography (GC). The GC apparatus (Perichrom Instrumentation, PR-2100) fitted with a flame ionization detector (FID) employed a capillary column (SGE E10, 25m × 0.53 mm i.d. × 1.0 μm) while N_2 was used as a carrier gas at a flow rate of 2 mL/min. The oven temperature was initially held at 120 °C for 3 min, increased to 240 °C at 5 °C min^{-1} and then held for 3 min. The injector and detector temperatures were 250 °C. A standard FAME mixture (RM-1, Supelco Ltd.) was used as an external standard for quantitative analysis of the FAME concentration [16].

2.7. FTIR analysis of FAME

The infrared spectra of FAME were analyzed by FTIR-BRUKER (Alpha) from 500 to 4000 cm^{-1}.

2.8. Experimental design

The experimental study on preparation of fly ash supported CaO catalyst and its application to synthesize biodiesel from soybean oil was performed through a face centered central composite design (FCCD) using Design Expert 8.0 software. The experimental design involved three process factors (independent variables) viz. CaO loading, catalyst concentration, methanol to oil molar ratio and one response (dependent variable) viz. % FAME yield. Based on the three level value by the software, two extreme points (highest and lowest) were used for each factor (10 and 30 wt.% of CaO loading (X_L), 1.0 and 5.0 wt.% of catalyst concentration (X_C) and 5.5 and 6.9 molar ratio for methanol to oil (X_{MR}) (Table 1). The coded values of independent variables can be found from the following equations:

$$x_L = \frac{X_L - 20}{10} \tag{2}$$

$$x_C = \frac{X_C - 3}{2} \tag{3}$$

$$x_{MR} = \frac{X_{MR} - 6.2}{0.7} \tag{4}$$

A two factor interaction (2FI) response surface equation was formulated by the software. A total of 15 different combinations were chosen in random order according to FCCD configuration for three factors (Table 2).

3. Result and discussion

3.1. Characterization of fly ash supported CaO catalyst

Fig. 1(a)–(c) exhibits the XRD patterns for the fly ash supported CaO catalyst samples developed in the range of 10–30% CaO loading respectively at the fixed calcination temperature of 1000 °C. It reveals the characteristic peaks of the crystalline phases of α-quartz, hematite and mullite representing the existence of major fly ash components and also depicting the presence of CaO crystalline phases. Typical reflections of CaO crystalline phase are observed only at 2θ = 37.4° [Fig. 1(b)] and 2θ = 64.4° [Fig. 1(a)] respectively. Whereas, the characteristics peaks corresponding to CaO crystalline phase are observed at 2θ = 32.2°, 37.4°,53.9° and 64.4° as shown in Fig. 1(c) corresponding to 30.0 wt.% CaO loading. Thus, the population of CaO phase in the fly ash supported catalyst frame work could be enhanced through increasing CaO loading.

Table 2
Central composite design layout for transesterification of soybean oil using fly ash supported CaO catalyst.

Run	Factor (X_L)	Factor (X_C)	Factor (X_{MR})	Response (Y_{FAME})
1	1.00	0.00	0.00	82.86
2	−1.00	−1.00	1.00	84.29
3	0.00	0.00	1.00	85.29
4	−1.00	1.00	−1.00	92.43
5	0.00	1.00	0.00	82.17
6	1.00	−1.00	1.00	96.99
7	−1.00	0.00	0.00	90.54
8	1.00	1.00	1.00	73.76
9	0.00	−1.00	0.00	86.51
10	−1.00	−1.00	−1.00	77.95
11	1.00	−1.00	−1.00	85.50
12	−1.00	1.00	1.00	87.19
13	0.00	0.00	−1.00	83.51
14	1.00	1.00	−1.00	74.25
15	0.00	0.00	0.00	86.97

At 30 wt.% CaO loading (Fig. 1(c)), the increased dispersion of CaO inhibited the sintering of Fe_2O_3 (hematite) which is evident from the absence of clear diffraction pattern corresponding to hematite crystallite phase and this is in accordance with [25]; while, at lower CaO loading (Fig. 1(a) and (b)) characteristics peak corresponding to hematite crystallite phase are observed, indicating lower dispersion of CaO into hematite phase.

However, catalyst samples with 30 wt.% CaO loading, depicted additional peaks of mullite (mainly Al_2O_3 and SiO_2) crystalline phase indicating strong interaction between Ca and Al_2O_3 and SiO_2 which is similar to the observation of Li et al. [31].

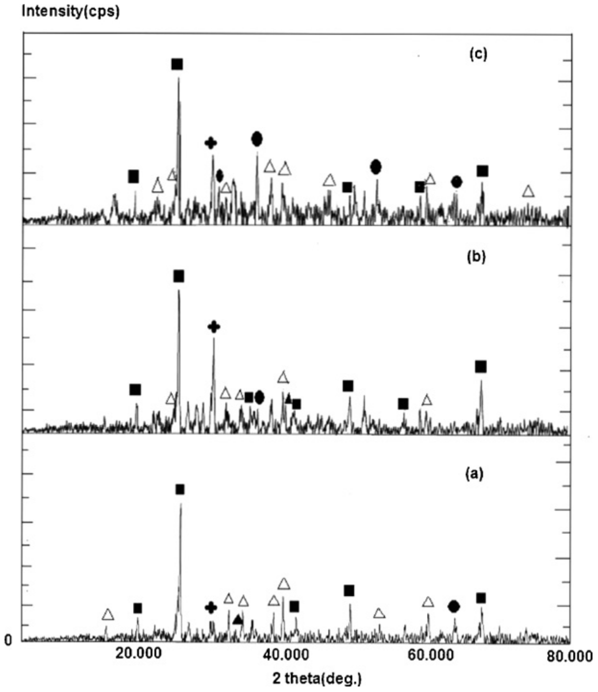

Fig. 1. Powder XRD patterns of fly ash based catalysts (a) 10 wt.% CaO, (b) 20 wt.% CaO and (c) 30 wt.% CaO [characteristic peaks due to CaO (●), α-Quartz (■), mullite (△), hematite (▲,) and dicalcium silicate (✚)].

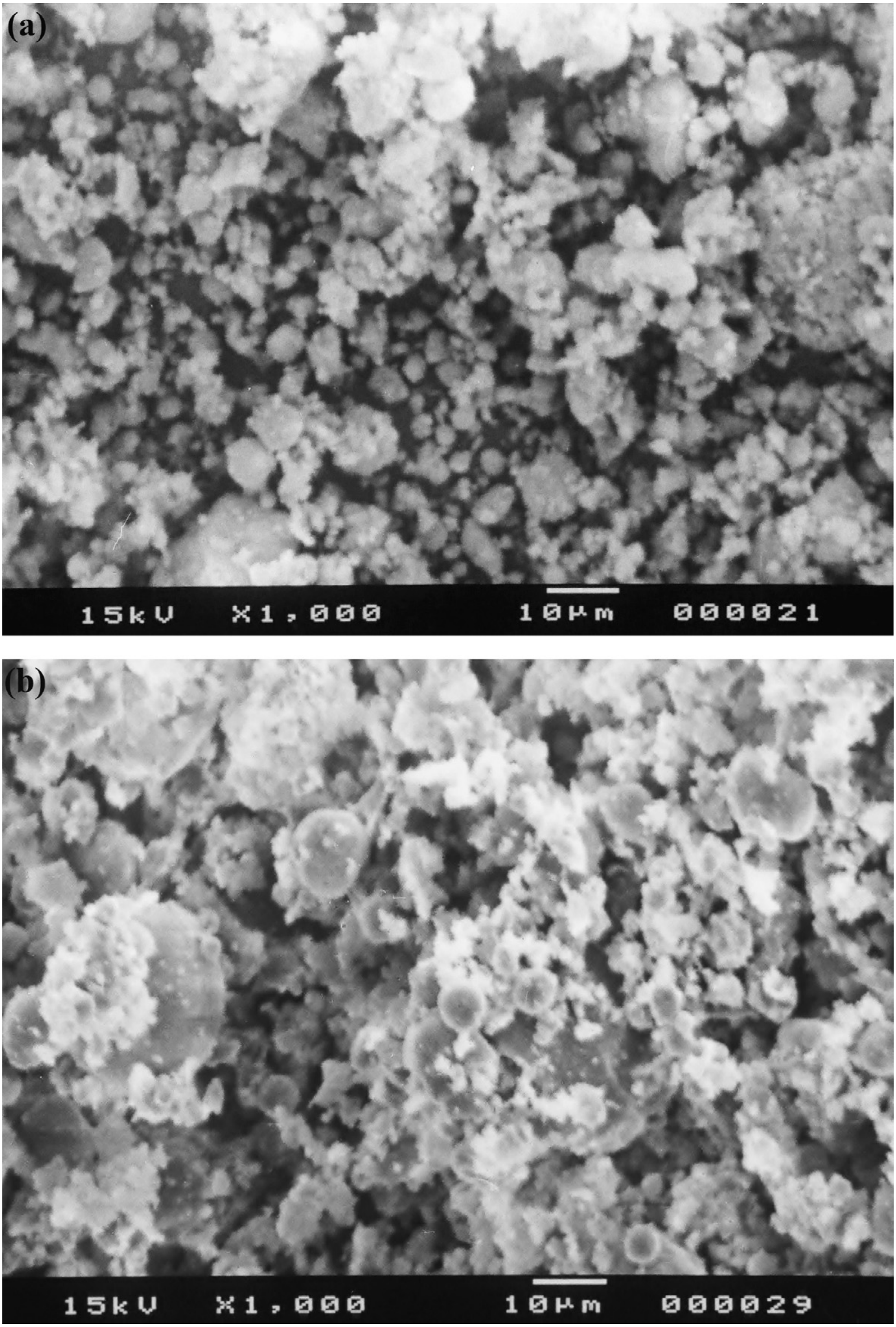

Fig. 2. SEM images of fly ash supported CaO catalyst (a) before calcination and (b) after calcination at 1000 °C under optimal i.e. 30 wt.% CaO loading.

The presence of dicalcium silicate (Ca_2SiO_4) crystalline phase was observed at $2\theta = 31.46^\circ$ in all the three catalysts with 10.0 wt.%, 20.0 wt.% and 30.0 wt.% CaO loading as depicted in Fig. 1(a), (b) and (c) respectively; this corroborates exactly with the findings of Jain et al. [24]. The formation of dicalcium silicate proceeds through the formation of dicalcium silicate hydrate ($Ca_2SiO_4 \cdot H_2O$) due to the reaction between main constituents of fly ash i.e. silica (SiO_2) with CaO in the presence of water during the wet impregnation preparation process of the catalyst as per the following "pozzolanic reaction" [32]

$$2CaO + SiO_2 + H_2O \rightarrow (CaO)_2(SiO_2)(H_2O)$$

During calcination for catalyst preparation at 1000 °C, dicalcium silicate (Ca_2SiO_4) is produced of dicalcium silicate hydrate ($Ca_2SiO_4 \cdot H_2O$) [33]. The presence of dicalcium silicate in the developed catalyst could facilitate rendering appreciable basicity of the developed catalyst due to the presence of Si–O–Ca bond [34].

The previous work on fly ash supported K_2O catalyst [25] for biodiesel synthesis did not report on SEM morphology. However, in our present study, the SEM images of the 30 wt.% CaO loaded fly ash supported catalyst before (Fig. 2(a)) and after calcination (Fig. 2b) are shown. The SEM micrograph reveals the agglomerated structure of the calcined catalyst demonstrating sintering of metal oxides upon heat treatment which is in reasonable agreement with Li et al. [31].

The Brunauer–Emmett–Teller (BET) method was applied to determine the specific surface area of the fly ash supported CaO catalyst capable of transesterifying soybean oil. The previous work on unsupported-CaO catalyst derived through direct calcination of waste egg shell [15] did not report on specific surface area of the catalyst and no attempt was made to prepare supported catalyst to enhance the surface area. In our work, fly ash supported CaO framework has been developed through wet impregnation method [25]. A specific surface area (S_{BET}) of 0.701 m^2/g was obtained corresponding to 30 wt.% CaO loading and calcination temperature of 1000 °C. The literature reported [25] fly ash supported K_2O base catalyst had BET surface area of $0.38 \pm 0.02\ m^2/g$. Thus, even with a variation of $\pm 0.02\ m^2/g$ in BET surface area measurement in the present investigation (due to possible experimental error), a surface area value of 0.721 or 0.681 m^2/g would be obtained; which corresponds to 89.73% or 79.21% higher BET surface area compared to the literature reported catalyst respectively. Thus, an improvement in BET surface area could be achieved in the present investigation indicating superior catalytic activity (high FAME yield) of the developed catalyst. The shape of the isotherm (Fig. 3(a)) depicting pore volume of the developed catalyst as a function of relative pressure (P/P_0) suggests that the fly ash supported CaO framework is essentially mesoporous solids (2–50 nm) and the isotherm for this material can be ascribed to type III of the IUPAC classification [35]. The type III is convex to the (P/P_0) axis over its entire range and therefore does not exhibit a point B. Isotherms of this type are not common, but there are a number of systems (e.g. nitrogen on polyethylene) which give isotherms with gradual curvature and an indistinct Point B. In such cases, the adsorbate–adsorbate interactions play an important role. In the present study, the BJH (Barret, Joyner and Halenda) [36] method which is most widely used for calculations of the pore size distributions over the mesopore and part of the macropore range has been applied to determine the catalyst pore volume of 0.0044 cm^3/g and modal pore size of the fly ash supported CaO catalyst is evaluated as 5.2 nm (inset of Fig. 3(a) shows differential pore size distribution).

Cumulative pore volumes of the developed catalyst are plotted vs. the log of pore diameter in (Fig. 3(b)). The plotted points approximately exhibit linear segments, designated in terms of pore diameter as follows: I, 3.5–15 nm; II, 15–80 nm; III, 80–180 nm;linear segments illustrate that pore diameters in these ranges have a logarithmetic normal distribution [37]. Linear segment I in Fig. 3(b) illustrates that 39.03% of the total catalyst pore volume is due to pores having diameters from about 3.5 to 15 nm; which represents mesoporous catalyst. Pore diameters in the range 15–80 nm (Fig. 3(b); segment II) contribute 43.24% of the total pore volume. About 17.73% of the total pore volume is associated with pore diameters in the size range 80–180 nm (Fig. 3(b); segment III). These large diameter pores will contribute most to triglyceride movement through catalyst pores. Thus, the developed catalyst exhibits a wide range of pore size distribution.

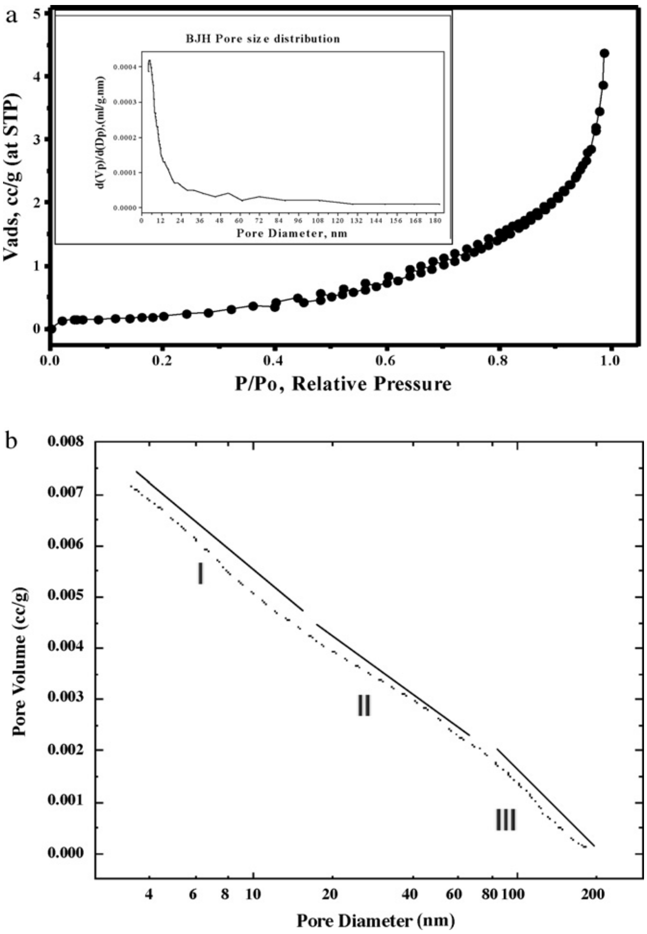

Fig. 3. (a) Pore volume vs. relative pressure (P/P_0) of fly ash supported CaO catalyst at optimal i.e. 30 wt.% CaO loading [inset: BJH differential pore size distribution for the determination of modal pore diameter of the catalyst]. (b) Cumulative pore volume vs. pore diameter of fly ash supported CaO catalyst at optimal i.e. 30 wt.% CaO loading showing pore size distribution.

The mean pore size of the developed catalyst is 5.2 nm, which may pose resistance related with the transport of the voluminous triglyceride molecules (for instance methyl oleate around 2.5 nm,) and glycerol molecules (around 0.6 nm) [38] through the nanopores. However, from the preceding discussion in Fig. 3(b), as the developed catalyst has significant pore volume corresponding to pore size much larger than 5.2 nm, hence, the developed catalyst is not expected to offer appreciable resistance to the movement of triglyceride/FFA molecules through the catalyst pores. The catalyst structure can, thus, facilitate obtaining high FAME yield.

The catalyst prepared in the present study possesses a basicity of 1.6 mmol HCl/g of catalyst; while CaO supported Al_2O_3 catalyst [30] with a basicity of 194 μmol/g could result 94% biodiesel yield. Thus, in the present study a relatively higher [30] basicity, relatively higher [25] and comparable [26] specific surface area of the devel-

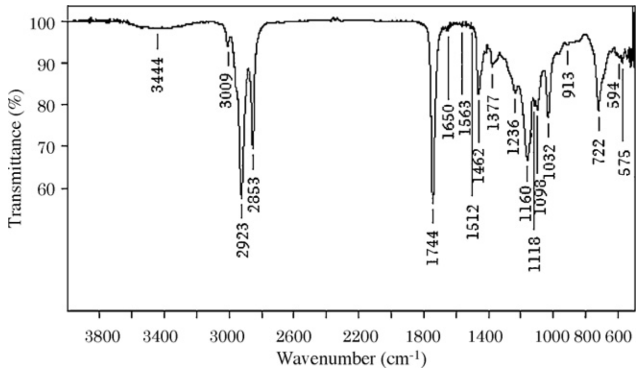

Fig. 4. FTIR analysis of FAME.

oped catalyst coupled with moderately high (5 h) reaction time is expected to render enhanced FAME yield.

3.2. Characterization of FAME by FTIR analysis

The infrared spectra of FAME (from soybean oil) are shown in Fig. 4. The strong ester peaks at 1744 cm^{-1} (the C=O vibration) and around 1160–1236 cm^{-1} (C–O vibrations) are clearly visible. The presence of traces of glycerol in the product biodiesel is reflected as peak at 1377 cm^{-1} which is similar to the observations of Knothe et al. [39]. The insignificant peak at 1118 cm^{-1} attributed to the C–CH_2–O vibration indicates reduced TG spectra in the product biodiesel. While, the very characteristic peak (1462 cm^{-1}) implies the presence of the CH_3 group in a mixture of FAME; which is consistent with Siatis et al. [40]. In addition, the small band seen at 3009 cm^{-1} (–HC=CH– stretching) represents low concentration of unsaturation in the product biodiesel. The presence of broad band at 3444 cm^{-1} in the sample is usually consistent with the stretch of the hydroxyl (–O–H) group and exhibited the existence of traces of water in the product due to inadequate drying during the purification of biodiesel.

3.3. Statistical analysis

In a previous study [25] on transesterification of sunflower oil using fly ash-based solid K_2O catalyst, no report has been made on the RSM optimization based on central composite design (CCD). However, in order to assess the effects of process variables on FAME yield (Y_{FAME}) and to evaluate the optimal process conditions corresponding to maximum FAME yield, RSM model based on FCCD with three factors viz. (X_L, X_C and X_{MR}) has been developed and validated in the present study. The experimental results showing Y_{FAME} as a function of process parameters (factors) tabulated according to FCCD are shown in Table 2. It is evident from the analysis of variance (ANOVA) (Table 3), that a two factor interaction (2FI) model was significant with a p-value (probability of error value) less than 0.0001 in predicting the Y_{FAME} values. The "Prob > F" value for the quadratic model was much higher (0.0011) than the 2FI model (<0.0001). The significant model terms (for 95% confidence intervals) with p-values less than 0.05 were X_L, X_C, X_{MR}, X_L X_C and X_C X_{MR}; while X_L X_{MR} were insignificant terms as their p-values were greater than 0.100.

Table 3
ANOVA results for yield of FAME corresponding to Eq. (5).

Source	Sum of squares	df	Mean square	F-Value	p-Value Prob > F
Model	519.30	6	86.55	25.62	<0.0001
X_L	36.25	1	36.25	10.73	0.0113
X_C	45.97	1	45.97	13.60	0.0061
X_{MR}	19.27	1	19.27	5.70	0.0440
X_LX_C	336.18	1	336.18	99.50	<0.0001
X_LX_{MR}	12.25	1	12.25	3.63	0.0934
X_CX_{MR}	69.38	1	69.38	20.53	0.0019
Residual	27.03	8	3.38	–	–
Cor. total	546.33	14	–	–	–

Statistical 'Model Fit Summary' ascertained the suitability of the 2FI model (Eq. (5)) compared to quadratic model as the sequential p-value for 2FI model is <0.0001 as compared to 0.1871 of quadratic model (Table 4). Also, the "Pred-R Squared" of 0.8014 for the 2FI model is in reasonable agreement with "Adj. R-Squared" of 0.9134. Moreover, the data values were closer to the unit slope in the 2FI model (Fig. 5) than in the quadratic model, where the values scattered and deviated away (figure not shown) implying that the 2FI model was the best model to represent the parametric effects on FAME yield. The 2FI model equation in terms of coded factors that represents the relationship between FAME yield (response) and process parameters (factors) is given by Eq. (5):

$$\begin{aligned} Y_{FAME} = {} & 84.68 - 1.90x_L - 2.14x_C + 1.39x_{MR} - 6.48x_Lx_C \\ & + 1.24x_Lx_{MR} - 2.94x_Cx_{MR} \quad (R2 = 0.9505) \\ & \times(-1 < x_L, x_C, x_{MR} < +1) \end{aligned} \tag{5}$$

The final equation in terms of actual factors:

$$\begin{aligned} Y_{FAME} = {} & 42.75845 - 0.31410X_L + 18.45264X_C + 4.75786X_{MR} \\ & - 0.32412X_LX_C + 0.17679X_LX_{MR} - 2.10357X_CX_{MR} \end{aligned} \tag{6}$$

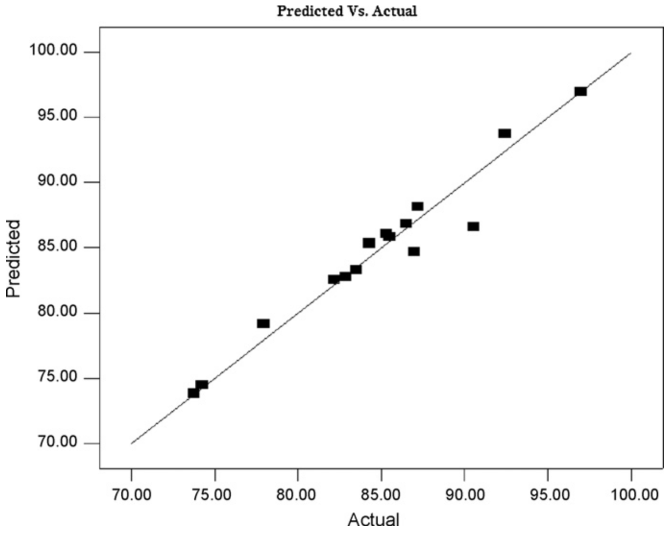

Fig. 5. Model fit profile of 2FI model.

Table 4
Model summary statistics of 2FI and quadratic model developed in case of biodiesel synthesis from soybean oil using fly ash supported CaO catalyst.

Source	Sequential p-value	Standard deviation	R-Squared	Adjusted R-squared	Predicted R-squared	Adeq. precision
2FI	<0.0001	1.84	0.95	0.91	0.80	18.43
Quadratic	0.1871	1.49	0.97	0.94	0.82	18.96

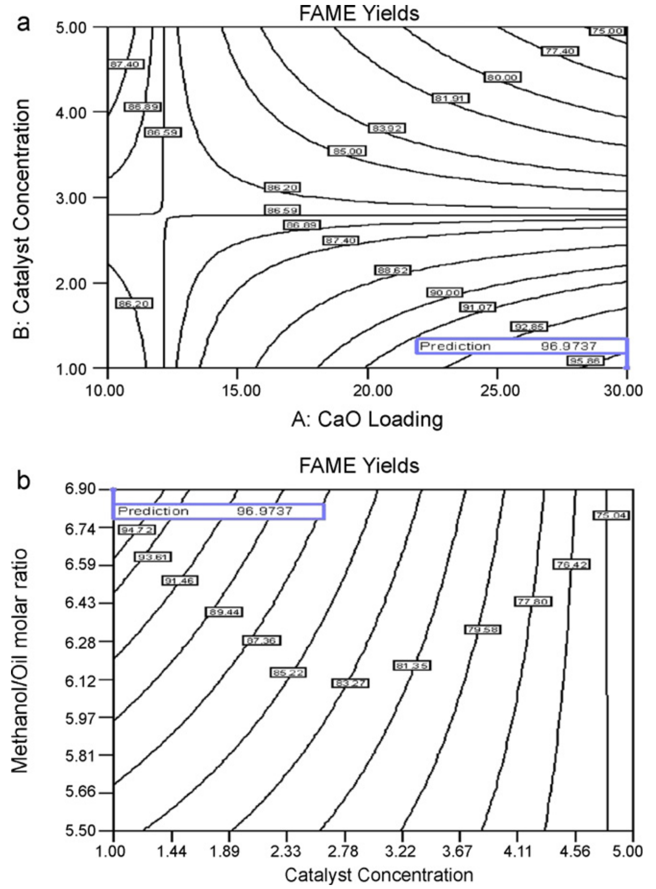

Fig. 6. Contour plots of FAME yield (a) effects of catalyst concentration and CaO loading at optimal value of methanol to oil molar ratio; (b) effects of methanol to oil molar ratio and catalyst concentration at optimal value of CaO loading.

Eq. (5) in coded values is used to study the effects of the variables on the response [30]. Positive sign in front of the terms indicates synergistic effect, whereas negative sign indicates antagonistic effect [41]. The model suggested catalyst concentration as the most important factor with a negative influence on FAME yield (Y_{FAME}). Methanol to oil molar ratio became the second important factor with a positive effect followed by CaO loading inversely affecting Y_{FAME}. The developed model equation has been validated using separate experimental results other than those used for FCCD.

3.4. Optimal process conditions

The optimal process conditions viz. CaO loading of 30 wt.%, catalyst concentration 1.0 wt.% of oil and 6.9:1 methanol to oil molar ratio that correspond to a maximum i.e. 96.97% FAME yield was determined through RSM. The biodiesel (FAME) yield obtained in this study is greater than that obtained applying K_2O/fly ash catalyst from sunflower oil [25].

As per the ANOVA (Table 3) the model significant interaction terms are X_LX_C and X_CX_{MR}. In order to reveal the interaction effects between X_L and X_C in influencing FAME yield at optimal value of X_{MR} the contour plot has been constructed (Fig. 6(a)). At the minimum catalyst concentration an increase in CaO loading enhances the FAME yield. While, at highest level of catalyst concentration, an increase in CaO loading decreases the FAME yield. Similarly, at the lowest CaO loading (surface reaction kinetics offers major resistance; the transesterification reaction rate is proportional to the available catalyst surface/concentration), an increase in catalyst concentration would increase FAME yield. At the highest CaO loading, an increase in catalyst concentration renders poor catalyst dispersion into reactant phases due to the moderately low stirring speed of 500 rpm (low mixing intensity) employed in the present study ensuing mass transfer as the major controlling resistance governing the transesterification reaction rate; resulting in a reduced FAME yield over 5 h operation.

At the optimal 30 wt.% CaO loading the interactions between methanol to oil molar ratio and catalyst concentration affecting FAME yield has been revealed through contour plot depicted in Fig. 6(b). At both minimum and maximum values of methanol to oil ratio an increase in catalyst concentration would decrease the FAME yield monotonically up to the highest catalyst concentration level encountered in the present study. As explained earlier, this can be attributed to the moderately low stirring speed of 500 rpm (low mixing intensity) [17,42]. On the contrary, at the lowest catalyst concentration of 1.0 wt.%, an increase in methanol to oil ratio would enhance FAME yield monotonically, as at this condition the transesterification becomes surface kinetics controlled instead of diffusion controlled owing to proper dispersion of catalyst into reactant phases. While, at the highest catalyst concentration value, a change in methanol to oil molar ratio would, however, have very little effect on FAME yield, which might be due to a mixing problem concerning solid catalyst and reactants [42].

3.5. Catalyst reusability

The reusability study on the developed fly ash supported CaO (egg shell derived) catalyst indicated repeated usability for about 16 times without major loss of activity for transesterification of soybean oil. The catalyst is also recyclable suggesting that this small amount of catalyst has sufficient stable basic sites for biodiesel synthesis. The catalyst started losing activity slowly after being used for more than 16 times and became completely deactivated after being used more than 18 times. Thus, the catalyst exhibited better performance compared to that of egg shell derived unsupported CaO catalyst [15]. The catalyst deactivation was attributed to the hydration of catalyst resulting from reaction with water (present in small amount in feed oil and methanol). Catalyst used more than 18 times, when analyzed in XRD, displayed reflections of $Ca(OH)_2$ conforming transformation of CaO due to hydration.

4. Conclusion

The fly ash supported CaO catalyst (derived from waste egg shell) developed in the present work, exhibited high catalytic performance in converting soybean oil into fuel grade biodiesel with a higher FAME content compared to minimum EN 14214, 2003 requirement of 96.5 wt.%. The optimal process conditions determined through response surface methodology (RSM) can be used for reactor scale up study. The industrial waste i.e. fly ash and municipal waste i.e. egg shell can thus be effectively utilized in developing low-cost, highly efficient supported base catalyst eventually creating an effective avenue of waste valorization for the generation of green energy.

Nomenclature

Y_{FAME}	FAME yield, %
W_b	Weight of biodiesel, g
p_{FAME}	Total wt.% of FAME in biodiesel, %
W_o	Weight of refined soybean oil, g
X_L	wt.% CaO loading
X_C	Catalyst concentration, wt.% oil
X_{MR}	Methanol to oil molar ratio

x_L	Coded value of CaO loading
x_C	Coded value of catalyst concentration
x_{MR}	Coded value of methanol to oil molar ratio

References

[1] K.G. Georgogianni, A.P. Katsoulidis, P.J. Pomonis, M.G. Kontominas, Transesterification of soybean frying oil to biodiesel using heterogeneous catalysts, Fuel Process. Technol. 90 (2009) 671–676.

[2] Z. Helwani, M.R. Othman, N. Aziz, J. Kim, W.J.N. Fernando, Solid heterogeneous catalysts for transesterification of triglycerides with methanol: a review, Appl. Catal. A: Gen. 363 (2009) 1–10.

[3] Y.M. Park, D.W. Lee, D.K. Kim, J.S. Lee, K.Y. Lee, The heterogeneous catalyst system for the continuous conversion of free fatty acids in used vegetable oils for the production of biodiesel, Catal. Today 131 (2008) 238–243.

[4] J. Jitputti, B. Kitiyanan, P. Rangsunvigit, K. Bunyakiat, L. Attanatho, P. Jenvanitpanjakul, Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts, Chem. Eng. J. 116 (2006) 61–66.

[5] S. Furuta, H. Matsuhashi, K. Arata, Biodiesel fuel production with solid super acid catalysis in fixed bed reactor under atmospheric pressure, Catal. Commun. 5 (2004) 721–723.

[6] B.-X. Peng, Q. Shu, J.-F. Wang, G.-R. Wang, D.-Z. Wang, M.-H. Han, Biodiesel production from waste oil feedstocks by solid acid catalysis, Process Saf. Environ. Prot. 86 (2008) 441–447.

[7] F.R. Abreu, D.G. Lima, E.H. Einloft-Ham, J.C. Rubim, P.A.Z. Suarez, New metal catalysts for soybean oil transesterification, J. Am. Oil Chem. Soc. 80 (2003) 601–604.

[8] S. Gryglewicz, Rapeseed oil methyl esters preparation using heterogeneous catalysts, Bioresour. Technol. 70 (1999) 249–253.

[9] N.A. Zafiropoulos, H.L. Ngo, T.A. Foglia, E.T. Samulski, W. Lin, Catalytic synthesis of biodiesel from high free fatty acid-containing feedstocks, Chem. Commun. (2007) 3670–3672.

[10] A. Kawashima, K. Matsubara, K. Honda, Development of heterogeneous base catalysts for biodiesel production, Bioresour. Technol. 99 (2008) 3439–3443.

[11] X. Liang, S. Gao, J. Yang, M. He, Highly efficient procedure for the transesterification of vegetable oil, Renew. Energy 34 (2009) 2215–2217.

[12] M. Zabeti, W.M.A.W. Daud, M.K. Aroua, Activity of solid catalysts for biodiesel production: a review, Fuel Process. Technol. 90 (2009) 770–777.

[13] M. Kouzu, T. Kasuno, M. Tajika, Y. Sugimoto, S. Yamanaka, J. Hidaka, Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production, Fuel 87 (2008) 2798–2806.

[14] X. Liu, H. He, Y. Wang, S. Zhu, X. Piao, Transesterification of soybean oil to biodiesel using CaO as a solid base catalyst, Fuel 87 (2008) 216–221.

[15] Z. Wei, C. Xu, B. Li, Application of waste eggshell as low-cost solid catalyst for biodiesel production, Bioresour. Technol. 100 (2009) 2883–2885.

[16] N. Nakatani, H. Takamori, K. Takeda, H. Sakugawa, Transesterification of soybean oil using combusted oyster shell waste as a catalyst, Bioresour. Technol. 100 (2009) 1510–1513.

[17] P.-L. Boey, G.P. Maniam, S.A. Hamid, Biodiesel production via transesterification of palm olein using waste mud crab (*Scylla serrata*) shell as a heterogeneous catalyst, Bioresour. Technol. 100 (2009) 6362–6368.

[18] N. Viriya-empikul, P. Krasae, B. Puttasawat, B. Yoosuk, N. Chollacoop, K. Faungnawakij, Waste shells of mollusk and egg as biodiesel production catalysts, Bioresour. Technol. 101 (2010) 3765–3767.

[19] E.S. Umdu, M. Tuncer, E. Seker, Transesterification of *Nannochloropsis oculata* microalga's lipid to biodiesel on Al_2O_3 supported CaO and MgO catalysts, Bioresour. Technol. 100 (2009) 2828–2831.

[20] M.C.G. Albuquerque, I.J. Urbistondo, J.S. Gonzalez, J.M.M. Robles, R.M. Tost, E.R. Castellon, A.J. Lopez, D.C.S. Azevedo, C.L. Cavalcante Jr., P.M. Torres, CaO supported on mesoporous silicas as basic catalyst for transesterification reaction, Appl. Catal. A: Gen. 334 (1–2) (2008) 35–43.

[21] M. Zabeti, W.M.Ai.W. Daud, M.K. Aroua, Optimization of the activity of CaO/Al_2O_3 catalyst for biodiesel production using response surface methodology, Appl. Catal. A: Gen. 366 (2009) 154–159.

[22] S. Benjapornkulaphong, C. Ngamcharussrivichai, K. Bunyakiat, Al_2O_3-supported alkali and alkali earth metal oxides for transesterification of palm kernel oil and coconut oil, Chem. Eng. J. 145 (2009) 468–474.

[23] K. Ojha, N.C. Pradhan, A.N. Samanta, Kinetics of batch alkylation of phenol with tert-butyl alcohol over a catalyst synthesized from coal flyash, Chem. Eng. J. 112 (2005) 109–115.

[24] D. Jain, C. Khatri, A. Rani, Fly ash supported calcium oxide as recyclable solid base catalyst for Knoevenagel condensation reaction, Fuel Process. Technol. (2010), doi:10.1016/j.fuproc.2010.02.021.

[25] M.S. Kotwal, P.S. Niphadkar, S.S. Deshpande, V.V. Bokade, P.N. Joshi, Transesterification of sunflower oil catalyzed by fly ash-based solid catalysts, Fuel 88 (2009) 1773–1778.

[26] A.K. Singh, S.D. Fernando, Transesterification of soybean oil using heterogeneous catalysts, Energy Fuels 22 (2008) 2067–2069.

[27] S. Gryglewicz, W. Piechocki, G. Gryglewicz, Preparation of polyol esters based on vegetable and animal fats, Bioresour. Technol. 87 (2003) 35–39.

[28] H. Noureddini, D. Zhu, Kinetics of transesterification of soybean oil, J. Am. Oil Chem. Soc. 74 (1997) 1457–1463.

[29] A. Bouaid, M. Martinez, J. Aracil, A comparative study of the production of ethyl esters from vegetable oils as a biodiesel fuel optimization by factorial design, Chem. Eng. J. 134 (2007) 93–99.

[30] M. Zabeti, W.M.A.W. Daud, M.K. Aroua, Biodiesel production using alumina-supported calcium oxide: an optimization study, Fuel Process. Technol. 91 (2010) 243–248.

[31] L. Li, S. Wang, Z. Zhu, X. Yao, Z. Yan, Catalytic decomposition of ammonia over fly ash supported Ru catalysts, Fuel Process. Technol. 89 (2008) 1106–1112.

[32] FernandezF J., J. Renedo, A. Garea, J. Viguri, J.A. Irabien, Preparation and characterization of fly ash/hydrated lime sorbents for SO_2 removal, Powder Technol. 94 (1997) 133–139.

[33] A. Yazdani, H.R. Rezaie, H. Ghassai, Investigation of hydrothermal synthesis of wollastonite using silica and nano silica at different pressures, J. Ceram. Process. Res. 11 (2010) 348–353.

[34] G.S. Pappas, P. Liatsi, I.A. Kartsonakis, I. Danilidis, G. Kordas, Synthesis and characterization of new SiO_2–CaO hollow nanospheres by sol–gel method: bioactivity of the new system, J. Non-Cryst. Solids 354 (2008) 755–760.

[35] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniewska, Reporting physisorption data for gas/solid systems with Special Reference to the determination of surface area and porosity (Recommendations 1984), Pure Appl. Chem. 57 (1985) 603–619.

[36] E.P. Barret, L.G. Joyner, P.H. Halenda, The determination of pore volume and area distributions in porous substances. 1. Computations from nitrogen isotherms, J. Am. Chem. Soc. 73 (1951) 373–380.

[37] M.M. Reddy, H.C. Claassen, D.W. Rutherford, C.T. Chiou, Welded tuff porosity and characterization using mercury intrusion nitrogen and ethylene glycol monoethyl ethersorption epifluorescence microscopy, Appl. Geochem. 9 (1994) 491–499.

[38] M.L. Granados, M.D.Z. Poves, D.M. Alonso, R. Mariscal, F.C. Galisteo, R. Moreno-Tost, J. Santamaria, J.L.G. Fierro, Biodiesel from sunflower oil by using activated calcium oxide, Appl. Catal. B: Environ. 73 (2007) 317–326.

[39] G. Knothe, Analyzing biodiesel: standards and other methods: a review, J. Am. Oil Chem. Soc. 83 (2006) 823–833.

[40] N.G. Siatis, A.C. Kimbaris, C.S. Pappas, P.A. Tarantilis, M.G. Polissiou, Improvement of biodiesel production based on the application of ultrasound: monitoring of the procedure by FTIR spectroscopy, J. Am. Oil Chem. Soc. 83 (2006) 53–57.

[41] B.H. Hameed, L.F. Lai, L.H. Chin, Production of biodiesel from palm oil (*Elaeis guineensis*) using heterogeneous catalyst: an optimized process, Fuel Process. Technol. 90 (2009) 606–610.

[42] Z. Yang, W. Xie, Soybean oil transesterification over zinc oxide modified with alkali earth metals, Fuel Process. Technol. 88 (2007) 631–638.