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Statistical optimization for lithium silicate catalyzed production of biodiesel from waste cooking oil

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Abstract−Lithium silicate is one of the suitable heterogeneous catalysts for biodiesel production. The possibilities of large number of combinations of different reaction parameters make the optimization of biodiesel production process over various heterogeneous catalysts highly tedious, necessitating the development of alternate strategies for parameter optimization. Here, Box-Behnken design (BBD) coupled with response surface methodology (RSM) is employed to optimize the process parameters required for the production of biodiesel from waste cooking oil using lithium silicate as catalyst. Simple method of impregnation was performed for the material preparation and the catalyst was analyzed using different techniques. It was found that the activity is directly proportional to the basicity data obtained from temperature programmed desorption (TPD) of CO_2 over various catalyst systems. The material exhibits macroporous morphology and the major crystalline phase of the most active catalyst was found to be Li_2SiO_3. The effects of different reaction parameters were studied and a biodiesel yield of 100% was obtained under the predicted optimum reaction conditions of methanol : oil molar ratio 15 : 1, catalyst amount 7 wt%, reaction temperature 55 °C and reaction time 2.5 h. The validation experiments showed a correlation coefficient of 0.95 between the predicted and experimental yield of biodiesel, which indicates the high significance of the model. The fuel properties of biodiesel obtained under the optimum conditions met the specifications as mentioned in ASTM D6751 and EN 14214 standards. Catalyst heterogeneity and low reaction temperature are the major attractions of the present biodiesel preparation strategy.

Keywords: Waste Cooking Oil, Lithium Silicate, Transesterification, Heterogeneous Catalysis, Response Surface Methodology, Biodiesel

INTRODUCTION

Energy crisis and environmental pollution are the major problems that the world currently faces [1-4]. Fossil fuels, the major source of energy in the world, are not only being depleted but are causing severe environmental pollution [5-7]. As a substitute for the petrodiesel, fuels derived from renewable bioresources are gaining increased momentum worldwide [8-10]. Biodiesel, the mono alkyl esters (mainly methyl ester) of long-chain fatty acids derived from vegetable oils or animal fats, is one of the promising renewable and greener fuels to be exploited [11,12].

The transesterification reaction of oils or fats catalyzed by acids or bases is the commonly employed process for the production of biodiesel [13]. Their corrosive and hazardous character, coupled with the low reaction rate, make the acid catalysts unsuitable for the production of biodiesel [14,15]. Also, separation of the homogeneous acid or base catalysts from the reaction mixture after the reaction involves several steps demanding high energy consumption [16,17]. Research on the use of eco-friendly alternative processes for the production of biodiesel is highly progressing [18]. The heterogeneous catalyzed transesterification reaction under mild conditions with higher yield is gaining increased focus. It avoids the major difficulties in the biodiesel separation and neutralization steps and also avoids high energy consumption during preparation being faced in the homogeneous catalyzed processes. Also, heterogeneous catalysts offer reusability [19-21].

Among the various heterogeneous catalysts, alkali metal loaded silica, zeolites, metal oxides, mesoporous materials, etc. have been widely investigated in biodiesel production [22-25]. In addition, alkaline earth metal oxides such as MgO and CaO have been used in the transesterification reaction [26,27]. There are many reports on heterogeneous catalysts based on lithium for the transesterification reaction to produce biodiesel. Wang et al. [28] reported that commercial Li_2CO_3 itself can be used as a catalyst in the transesterification of soybean oil. The reaction results in an oil conversion of 97.2% under the optimal reaction conditions of catalyst weight 12 wt%, methanol : oil molar ratio 32 : 1 at a reaction temperature of 65 °C for 2 h reaction. The reusability of the catalyst was investigated for ten repeated cycles and the catalyst was found to be stable, yielding 89.1% biodiesel after 9th cycle of reaction suggesting the stability of the catalyst in the reaction. Chen et al. [29] studied the application of a lithium based heterogeneous catalyst prepared

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from silica derived from rice hush ash (RHA) for the transesterification of soybean oil with methanol. The XRD pattern of the catalyst suggested the formation of Li_2SiO_3 as the active phase in the catalyst. 99.5% conversion was obtained under the best reaction conditions determined from different experiments as 4 wt% catalyst amount, reaction temperature of 65 °C, methanol : oil molar ratio of 24 : 1 for 3 h reaction. The catalyst is reusable for five times giving FAME content of 86.7% in the 5th cycle. Lithium orthosilicate heterogeneous catalyst prepared from Li_2CO_3 and rice husks is used as catalyst for biodiesel production [30]. A biodiesel conversion of 98.8% was obtained under the optimal reaction conditions. The catalyst was found to be effectively reusable. Wang et al. [31] synthesized lithium orthosilicate (Li_4SiO_4) using a solid-state reaction between lithium nitrate and silica, and evaluated the catalytic activity in the transesterification of soybean oil. The catalyst is highly efficient in the transesterification giving 98.1% conversion to biodiesel under the optimal reaction condition of methanol : oil molar ratio of 18 : 1, 6 wt% catalyst amount, temperature at 65 °C for 2 h reaction. The rice husk silica has also been used as the support material for the preparation of lithium silicate, which is used for the transesterification of used cooking oil with methanol [32]. The catalysts were prepared by the impregnation method. The optimum conditions for the transesterification reaction were suggested as catalyst amount 3 wt%, methanol : oil molar ratio 9 : 1, reaction temperature of 65 °C and time 3 h at which a conversion of 96.6% is obtained. Cement was used as a heterogeneous silicate catalyst in the transesterification of soybean oil using methanol [33]. The maximum methyl ester conversion of 98.5% was obtained under the methanol : oil molar ratio of 24 : 1 at 65 °C temperature for 3 h when 32.8 wt% catalyst was used for the reaction. Catalyst leaching is the main problem observed in the cement catalyst because the cement species in the presence of methanol shows homogeneous catalysis, which is responsible for the catalytic activity. The decrease in catalytic activity is also due to the formation of calcium glyceroxide from CaO and glycerol, which get adsorbed on the solid surface. The first report on the use of $LiAlO_2$ as a heterogeneous catalyst was done by Dai et al. [34]. The catalyst is prepared by the solid state mixing method by using Li_2CO_3 and Al_2O_3 in a 4 : 1 mol ratio. The incorporation of lithium into the alumina surface increases the number of active basic sites which is responsible for the activity of the catalyst. Under the reaction conditions of methanol : oil molar ratio of 24 : 1, temperature 65 °C, catalyst weight 6 wt% and reaction time 2 h, maximum biodiesel conversion of 97.5% was obtained. Biodiesel production using lithium titanate catalyst is reported by Chen et al. [35]. Li_2TiO_3 was prepared from titania powder and Li_2CO_3 by the solid state mixing method. The optimal reaction conditions obtained were methanol : oil molar ratio 24 : 1, catalyst amount 6 wt%, and a reaction temperature of 65 °C for 2 h. The maximum biodiesel conversion obtained under this condition was 98.5%. Waste silicon has been used as the silica source for the preparation of a base catalyst and is employed in biodiesel production [36]. Silicon is converted to silica by high temperature heating and is used as the support material for incorporating the active species, Li_2CO_3, by the solid state mixing method. The higher activity of lithium modified silica than that of pure silica is attributed to the higher base strength. Li_4SiO_4 is the active phase that takes part in the catalytic process of biodiesel production. A maximum conversion of 99.04% was observed at the optimal reaction conditions of methanol : oil molar ratio 12 : 1, 6 wt% catalyst amount at a reaction temperature of 62 °C for 3 h reaction. Lithium silicate has been used as the catalyst for the transesterification reaction of algal oil to produce biodiesel [37]. The transesterification results in a biodiesel conversion of 76.2% under a reaction temperature 68 °C with a catalyst amount of 3 wt% at a methanol : oil molar ratio 18 : 1 for a reaction time of 4 h.

As is evident from the literature data, normally, the methanol : oil molar ratio, weight of the catalyst, time, as well as the reaction temperature of the reaction mixture are the variable reaction parameters affecting the yield of biodiesel. The conventional one-to-one optimization strategy for all these parameters in obtaining a suitable condition with the maximum yield is a tedious process, since a large number of combinations would be involved in the process [38]. Therefore, in the present work, we preferred to use response surface methodology (RSM), the statistical optimization technique for the present heterogeneous catalyzed biodiesel production process. RSM is a widely used mathematical-*cum*-statistical technique being employed for the optimization, modeling and analysis of the yield of biodiesel [39-42]. Box Behnken design (BBD) is one of the most common designs in optimization studies, which in combination with RSM technique was applied here for the optimization of different variables so as to attain the maximum efficiency in the lithium silicate catalyzed process of the production of biodiesel [43,44]. To the best of our knowledge, there are no reports on the use of RSM strategy for the optimization of lithium silicate catalysed biodiesel production.

The present work aims at the effective production of fatty acid methyl esters by the transesterification of waste cooking oil with methanol using lithium silicate as the catalyst. Thus, the specific objectives set in this study were: (a) preparation of lithium silicate, (b) characterization of the best lithium based catalyst, (c) optimization of reaction parameters for the biodiesel production, and (d) reusability studies of the catalyst so as to attain better performance under mild reaction conditions compared to the existing methods of biodiesel production over lithium based catalysts.

EXPERIMENTAL

1. Materials

Analytical grade chemicals such as silica (Sigma Aldrich chemicals), lithium nitrate, methanol (Nice Chemicals Pvt. Ltd. India) were used. Waste cooking oil was collected from the nearby hotels, and filtered to remove the solid impurities, and was then subjected to processes such as degumming [45] followed by acid pretreatment [46] for use in biodiesel production experiments. The detailed procedures for the degumming and pretreatment are provided in experimental section S1 and S2 respectively (supplementary information).

2. Catalyst Preparation

The catalysts were prepared by incipient wet impregnation method using aqueous solution of $LiNO_3$. Impregnation was done over SiO_2 support at varying Li : Si molar ratios. The $LiNO_3$-SiO_2 mixture was then stirred using a mechanical stirrer with an rpm of 800 at 90 °C for 6 h. The dried mixture was then kept in a hot air oven at 90 °C for overnight. Calcination was at 650 °C for 3 h to obtain the lithium silicate catalyst. Different catalytic systems were also prepared by varying the Li : Si molar ratios such as 10 : 90, 20 : 80, 30 : 70, 40 : 60, 50 : 50 and 66.66 : 33.33. The systems were designated as Li : Si (m : n), where m : n indicates the molar ratio of Li : Si in the catalyst. For simplicity, Li : Si (66.66 : 33.33) is further designated as Li : Si (2 : 1).

3. Catalyst Characterization

The catalyst system, Li : Si (2 : 1) was characterized by different techniques. Fourier Transform Infrared (FTIR) spectrum of Li : Si (2 : 1) was recorded by using Jasco FTIR (4100) spectrometer. The X-ray diffraction (XRD) pattern of catalyst was recorded using Rigaku Mini flex 600 diffractometer. The morphology of the catalyst was investigated with a JEOL Model JSM-6390LV Scanning Electron Microscope (SEM) and the JEOL model JEM-2100 Transmission electron microscope (TEM). The inductively coupled plasma absorption emission spectroscopy (ICP-AES) analysis was performed by Thermo Electron IRIS INTREPID II XSP DUO in the spectral range 165 to >1,000 nm of resolution 0.005 nm at 200 nm to determine the percentage of Li and Si in the catalyst. The basicity of the different catalyst systems was studied by temperature programmed desorption (TPD) of CO_2 using a conventional flow reactor.

4. Biodiesel Preparation

A definite amount (5 g) of waste cooking oil was taken in a 50 ml RB flask fitted with a water condenser and kept in an oil bath. In a typical procedure, the catalyst was (6 wt% of oil) added to the oil and the reaction mixture was heated to 65 °C while stirring at 500 rpm using a magnetic stirrer under atmospheric pressure. As the temperature reached 65 °C, methanol was added to the reaction mixture at a specified methanol : oil molar ratio of 15 : 1 and was again stirred for 2 h. After the transesterification reaction, the reaction mixture was subjected to centrifugation for 5 min at a speed of 1,000 rpm to separate the catalyst. The liquid part containing fatty acid methyl ester (FAME), unreacted oil, methanol and the other products were transferred to a separating funnel for separating biodiesel from glycerol. The glycerol that settled at the bottom due to higher density than biodiesel was separated. The biodiesel in the separating funnel was washed with hot deionized water (10 ml) thrice. Deionized water was used for removing the unreacted alcohol, glycerol and any leached out catalyst present in the biodiesel [47]. After washing, the water at the lower part of separating funnel was separated and the biodiesel was taken into a centrifuge tube. Then, anhydrous sodium sulphate (about 1 g) was added to the biodiesel and centrifuged for 10 min at a speed of 1,000 rpm to remove the remaining water [48]. The pure biodiesel obtained was filtered using a filter paper and subjected to GC analysis (after derivatization using MSTFA) for the determination of FAME content using a Thermofisher Trace GC 700 gas chromatograph. Details of biodiesel analysis are given in the experimental section, S3 (supplementary information).

5. Experimental Design for Transesterification and Statistical Analysis by RSM

Box-Behnken design (BBD), the experimental design selected for the present study, helps in understanding the effects of the four different reaction parameters on the FAME content in the transesterification of waste cooking oil over lithium silicate catalyst, Li : Si (2 : 1). The design of experiment for the transesterification of waste cooking oil was established using the software Minitab version 14 (Minitab USA) [49]. The optimization of different reaction parameters that affect the methyl ester yield during the transesterification process was done by applying the principles of RSM. BBD was used along with RSM to understand the existence of interactions among the variables and the responses. The model used here was for deducing a mathematical correlation between different independent variables on the FAME content.

Table 1. Experimental range and levels of the independent variables used in the study

Variables	Range and levels		
	−1	0	+1
Methanol : oil molar ratio	9 : 1	12 : 1	15 : 1
Catalyst amount (wt%)	5	6	7
Reaction time (h)	1	2	3
Reaction temperature (°C)	45	55	65

The reaction parameters chosen for the design of experiments were temperature, catalyst weight, reaction time and methanol:oil molar ratio. Stirring speed was kept constant as 500 rpm in all the experimental trials and the reactions were conducted at atmospheric pressure. The levels and range of the four variables were selected based on the literature reports [50-52], properties of reactants and the preliminary studies that were carried out in the laboratory. The three levels, *i.e.*, high (+1), medium (0) and low (−1), values of reaction variables are illustrated in Table 1. The biodiesel conversion at room temperature was negligible over the present catalyst. Therefore, it was not taken as the lower temperature limit. 15 : 1 was selected as the maximum methanol : oil molar ratio, because this is the point at which maximum conversion of 100% was obtained. 9 : 1 was selected as the lower limit since below this limit only a small amount of FAME was obtained. Similar is the case for the selection of catalyst weight as well as reaction time.

Based on these high, medium and low values, 27 experimental trials were assigned. All the trials were carried out in duplicate and the results were analyzed by fitting the data to a second order polynomial Eq. (1).

$$Y = \beta_0 + \Sigma_{i=1}^{k}\beta_i X_i + \Sigma_{i=1}^{k}\beta_{ii} X_i X_i + \Sigma_{i=1}^{k}\Sigma_{j=1}^{k}\beta_{ij} X_i X_i,\ i<j \qquad (1)$$

where, Y represents the response variable; β_0 is the interception coefficient; β_i is the coefficient of the linear effect; β_{ii} is the coefficient of quadratic effect; β_{ij} is the coefficient of interaction effect when i<j, and k is the numbers of variables involved in the experiment. Regression analysis of the data was carried out by using the same software by fitting it to the second order polynomial Eq. (1), and thus evaluates the significance of the model by statistical analysis.

The validity of quadratic model was checked by carrying out four different experiments as predicted by the point prediction software, Minitab 14. The influence of the catalyst in the production of biodiesel by the way of RSM mediated optimization was compared with the obtained values. The value of regression and correlation coefficients can indicate the significance and validity of

Table 2. TPD of CO_2 results of the catalysts

Sl. no.	Catalyst system	Basicity distribution ($mmolg^{-1}$)			Total
		Weak (RT-200 °C)	Medium (200 °C-400 °C)	Strong (400 °C-700 °C)	(RT-700 °C)
1	SiO_2	0.0	0.0	0.0036	0.0036
2	Li : Si (10 : 90)	0.0	0.0002	0.00	0.0060
3	Li : Si (20 : 80)	0.0	0.0	0.012	0.0120
4	Li : Si (30 : 70)	0.0	0.0006	0.0129	0.0135
5	Li : Si (40 : 60)	0.0009	0.011	0.0305	0.0424
6	Li : Si (50 : 50)	0.0037	0.1989	0.0471	0.2497
7	Li : Si (2 : 1)	0.0	0.2493	0.1186	0.3679

the model for this optimization.

6. Reusability of the Catalyst

After the reaction under optimized condition as predicted by the model, the catalyst was separated from the reaction mixture by filtration and washed several times with methanol. The catalyst was then dried at 90 °C, activated at 650 °C for 1 h, and used for subsequent runs for the biodiesel production under optimized reaction conditions.

RESULTS AND DISCUSSION

Statistical optimization of reaction variables for biodiesel production over lithium silicate catalyst was carried out successfully. To determine the desired loading of $LiNO_3$ over SiO_2, so as to obtain the best catalyst, a series of catalysts were prepared by varying the

Table 3. Effect of Li : Si molar ratio on the FAME content

Sl. no.	Catalyst system	Li : Si molar ratio	FAME (%)
1	Li : Si (10 : 90)	10 : 90	14.62
2	Li : Si (20 : 80)	20 : 80	23.64
3	Li : Si (30 : 70)	30 : 70	55.19
4	Li : Si (40 : 60)	40 : 60	80.03
5	Li : Si (50 : 50)	50 : 50	99.98
6	Li : Si (2 : 1)	66.66 : 33.33	100

Reaction conditions: 6 wt% catalyst, 15 : 1 methanol : oil molar ratio, reaction temperature of 65 °C and reaction time of 2 h

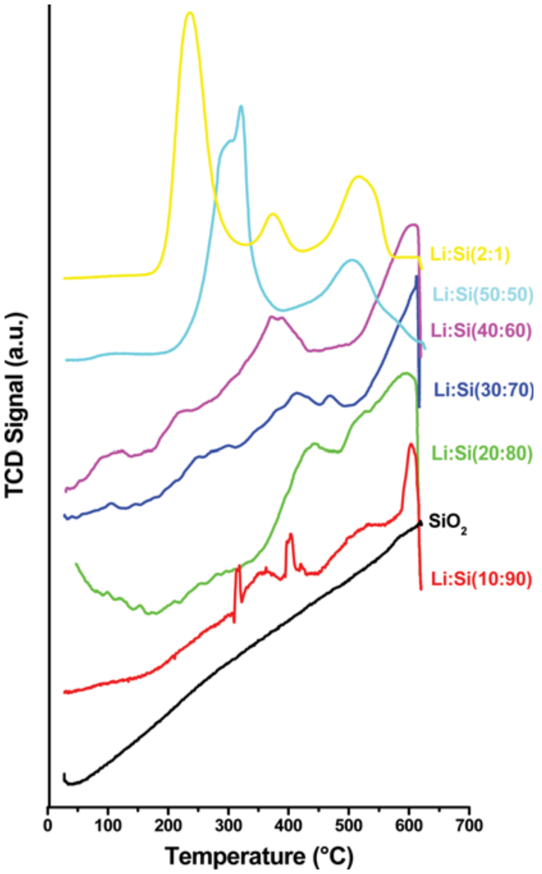

Fig. 1. TPD of CO_2 profiles on the support and lithium silicate catalysts.

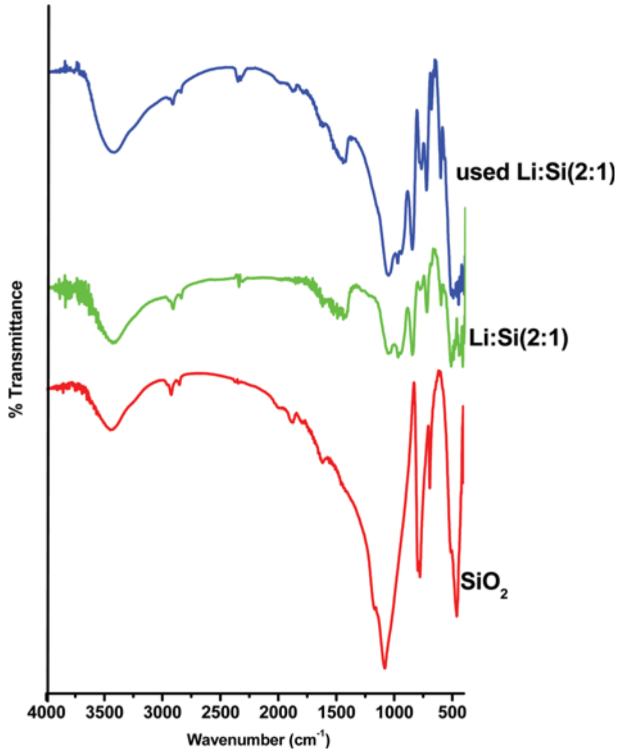

Fig. 2. FTIR spectra of SiO_2, Li : Si (2 : 1) and used Li : Si (2 : 1) catalysts.

Li : Si molar ratios. The basicity of the prepared systems was investigated using TPD of CO_2 since lithium silicate is a base catalyst used in biodiesel production. The total basicity measurements carried out by TPD of CO_2 for all catalysts are summarized in Table 2 and the CO_2-TPD profiles are given in Fig. 1. The peaks present around room temperature (RT) to 200 °C are assigned to desorption of CO_2 physisorbed or adsorbed on weakly basic sites. The peaks around 200 °C to 400 °C are ascribed to desorption of CO_2 adsorbed on moderately basic sites. The peaks above 400 °C are assigned to CO_2 adsorbed on strongly basic sites. The basicity measurement indicates that silica possesses negligible basicity, and basicity is enhanced upon lithium loading. As the amount of lithium increases, the total basicity also increases and reaches a maximum value of 0.3679 $mmolg^{-1}$ in the case of Li : Si (2 : 1) catalyst.

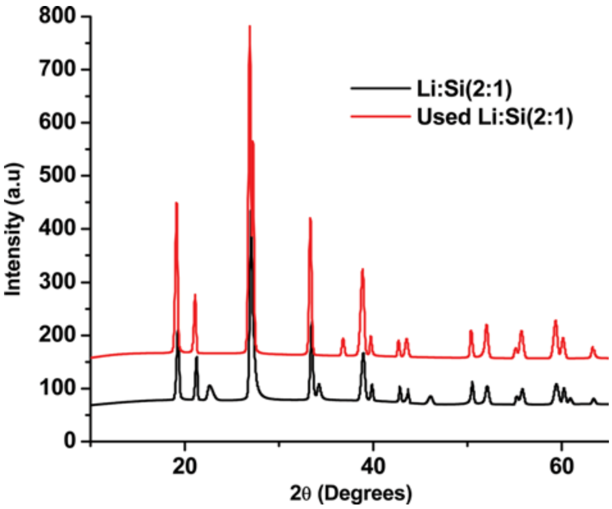

Fig. 3. XRD pattern of Li : Si (2 : 1) and used Li : Si (2 : 1) catalysts.

An initial activity study was conducted over different catalysts to find the most efficient system for the biodiesel production. The reaction conditions chosen were based on previous reports and experiments conducted in the laboratory. The obtained FAME content for each reaction is given in Table 3. It was found that the activity of different systems was in good correlation with basicity data obtained from TPD of CO_2. In the case of Li : Si (50 : 50), a conversion of 99.98% was obtained. But this catalyst was not much reusable, and the activity dropped to 85.6% in the first cycle

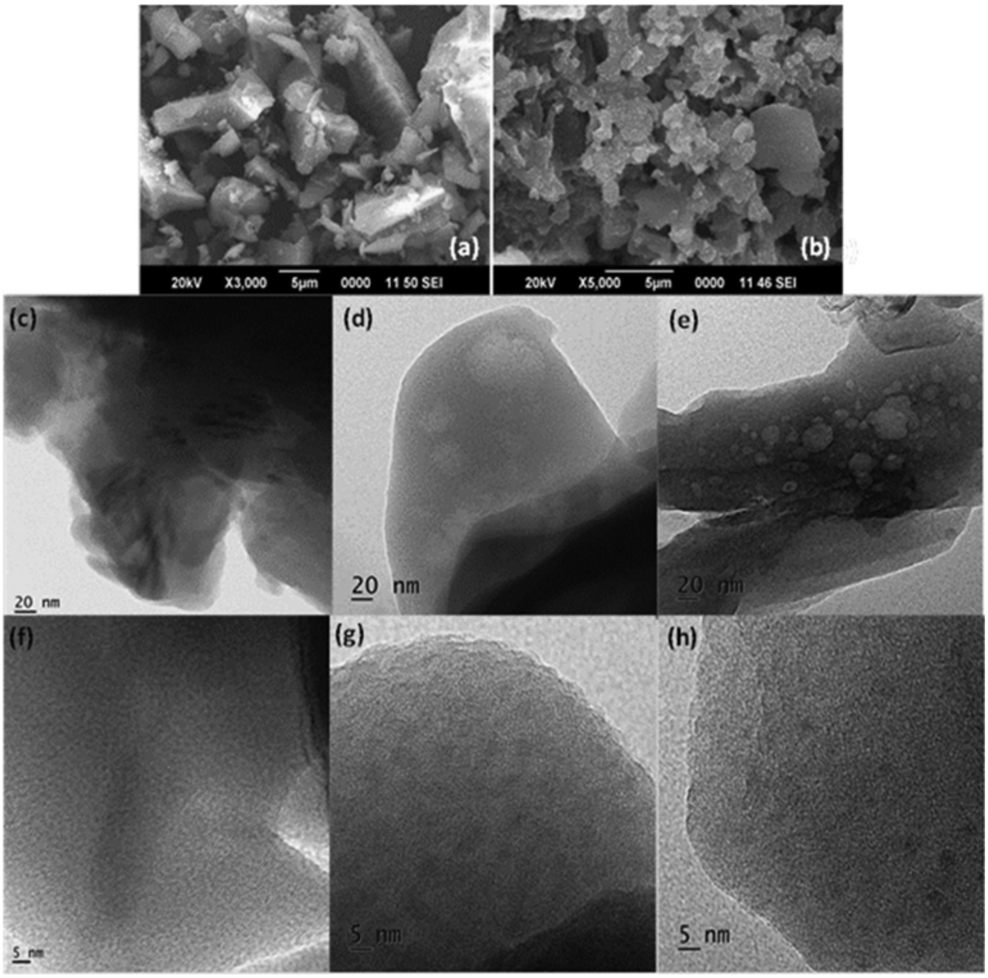

Fig. 4. SEM, TEM and high resolution TEM photographs of silicon dioxide [(a), (c) and (f)], lithium silicate [(b), (d) and (g)] and used catalysts [(e) and (h)].

itself. Since the international standard specification (EN14214) of FAME content is 96.5%, the catalyst was not found to be suitable for biodiesel production. At a Li : Si molar ratio of 2 : 1, the catalyst was found to be effectively reusable yielding 98.5% FAME in the second cycle. Hence, the system Li : Si molar ratio of 2 : 1 was chosen for further optimization studies. The reactions over other catalyst systems yielded lower FAME content, some amount of mono and diglycerides are also formed. The above catalyst was characterized using FTIR spectroscopy, XRD, SEM, ICP-AES and TEM to investigate the structural and textural properties of the system to correlate with its catalytic activity.

1. Catalyst Characterization

The identification of different functional groups present in the Li : Si (2 : 1) catalyst as well as in silica was done by the FTIR spectral analysis (Fig. 2). In the spectra, the broad band centered at 3,560 cm^{-1} corresponds to the stretching vibration of -OH groups from adsorbed water [53]; the bands located at 962 cm^{-1} and 906 cm^{-1} were due to the asymmetric stretching vibration of Si-O-H silanol groups and bending vibration of O-Si-H, respectively; and also, bands of O-Si-O and Si-O-Si bridges are seen around 800 cm^{-1} [54]. The absorption peaks in the spectra of silica at about 794 cm^{-1} and 1,100 cm^{-1} correspond to the O-Si-O stretching vibration [32]. The absorption band at about 1,623 cm^{-1} corresponds to the bending vibration of water molecules that are bound to the catalyst surface [55,56]. The absorption bands that originated as a result of Li-O bond vibration are at about 445-611 cm^{-1} in the lithium silicate sample [32]. The absorption bands corresponding to Li-OH vibration and Si-O-Li vibration are at 855 cm^{-1} and 965 cm^{-1}, respectively, in the spectra of Li : Si (2 : 1) [32]. The O-Si-O stretching vibration observed at 1,100 cm^{-1} and 794 cm^{-1} in SiO_2 [32] is shifted to 1,060 cm^{-1} and 785 cm^{-1} in the FTIR spectrum of the Li : Si (2 : 1) catalyst. This may be due to the interaction between the Lithium and silica.

The crystalline nature of the catalyst was investigated by X-ray diffraction analysis (Fig. 3). The characteristic peaks at 2θ values of about 18.9°, 26.9°, 33.2°, 38.7°, 43.2°, 51.9°, 55.2° and 59.1° correspond to the diffraction from (020), (111), (130), (131), (221), (132), (241) and (330) crystal planes of Li_2SiO_3 [57-60]. Weak diffraction from $Li_2Si_2O_5$ phase is also observed at 2θ value corresponding to 22.2° [58].

The surface morphology of Li : Si (2 : 1) was investigated using SEM. The SEM images of pure silicon dioxide and the developed lithium silicate are shown in Fig. 4. From Fig. 4(a), it is clear that silica exhibits a flake-like morphology. A drastic change in the morphology is observed for silica upon incorporation of lithium (Fig. 4(b)). Similar to other biodiesel catalysts reported, here also the catalyst showed a macroporous morphology throughout the surface, which could enhance the production of biodiesel. Several

Table 4. Experimental trials according to Box-Behnken design for optimizing lithium silicate catalyzed transesterification

Run order	Temperature (°C)	Time (h)	Methanol/oil molar ratio	Catalyst weight (wt%)	Observed FAME (%)	Expected FAME (%)
1	55	3	9	6	95.15	98.42
2	45	2	9	6	83.89	76.54
3	65	2	12	7	99.3	99.07
4	55	2	12	6	95.79	96.24
5	55	1	12	7	96.55	90.8
6	55	2	15	5	83.04	88.47
7	45	1	12	6	72.64	74.57
8	55	2	12	6	96.1	96.24
9	55	2	15	7	99.27	100
10	55	1	9	6	62.72	70.03
11	55	1	15	6	98.56	97.43
12	65	2	9	6	97.05	90.28
13	65	2	15	6	100	98.57
14	55	3	12	5	99.06	96.04
15	45	2	15	6	93.85	91.84
16	45	2	12	5	78.92	81.29
17	55	2	9	7	83.03	84.21
18	55	3	12	7	99.74	97.57
19	55	1	12	5	83.87	77.26
20	55	2	12	6	96.85	96.24
21	45	2	12	7	85.01	87.67
22	65	3	12	6	92.9	97.59
23	65	2	12	5	90.89	90.37
24	55	2	9	5	81.89	84.22
25	45	3	12	6	92.03	94.41
26	65	1	12	6	87.65	91.88
27	55	3	15	6	99.78	94.61

researchers reported the usage of macroporous catalysts in the transesterification reaction for producing biodiesel with high yield [61-63]. TEM images and high resolution TEM photographs of silica and Li : Si (2 : 1) are shown in Fig. 4(c) and (f) and (d) and (g), respectively, which further confirms the porous nature of the synthesized catalyst.

The ICP-AES analysis of Li : Si (2 : 1), the best catalyst, was carried out to determine the composition of the catalyst, and the results reveal that the Li : Si ratio is 2 : 1, which supports the existence of the catalyst in the form of Li_2SiO_3 as suggested from x-ray diffraction analysis.

2. Statistical Optimization of Reaction Parameters

Based on the preliminary experiments, different reaction parameters were selected for the transesterification reaction. Initially, the transesterification reaction was carried out with used cooking oil under the reaction conditions of catalyst weight of 6 wt%, methanol : oil molar ratio 15 : 1, reaction temperature 65 °C and reaction time 1 h. We obtained fuel grade biodiesel under these conditions. But, the FAME content was only 96.93%. To obtain better yields, the reaction time was increased to 2 h. At this condition, the maximum FAME content of 100% was obtained. The FAME content remained as 100% at a reaction time of 3 h, as expected. Thus, 2 h was taken as the medium value of reaction time and 3 h as the higher reaction time. This is to obtain higher FAME content under low catalyst weight, reaction temperature and methanol : oil molar ratio.

Temperature, methanol : oil molar ratio, and weight of the catalyst are the other prominent variables affecting the transesterification process for the biodiesel production. All these variables were subjected to BBD analysis, followed by RSM to find the optimum conditions in maximizing the production of biodiesel; accordingly, a set of 27 experiments was performed (Table 4). The results, which were analyzed by the analysis of variance (ANOVA), showed that the predicted and experimental values for FAME content did not show significant difference, and thus the accuracy of the model is confirmed. A second-order polynomial equation was fitted to the optimization of biodiesel production, which resulted in the following regression Eq. (2):

$$\begin{aligned}Y=&-338+5.67\,X_1+86.7\,X_2+11.4\,X_3+26.5\,X_4\\&-0.0372\,X_1{*}X_1-2.91\,X_2{*}X_2-0.357\,X_3{*}X_3-2.92\,X_4{*}X_4\\&-0.353\,X_1{*}X_2-0.0584\,X_1{*}X_3=0.058\,X_1{*}X_4\\&-2.601\,X_2{*}X_3-3.00\,X_2{*}X_4+1.257\,X_3{*}X_4\end{aligned}\qquad(2)$$

where, Y=FAME content, X_1=reaction temperature, X_2=reaction time, X_3=methanol : oil molar ratio, and X_4=catalyst weight. Based on the results, the model was used to generate response surfaces for the analysis of the variable effects on the production of biodiesel. The response surface and contour plots generated using Eq. (2) are depicted in Fig. 5 and Fig. 6, respectively.

The significance, precision and fitness of the model for this optimization process were determined from the ANOVA table (Table

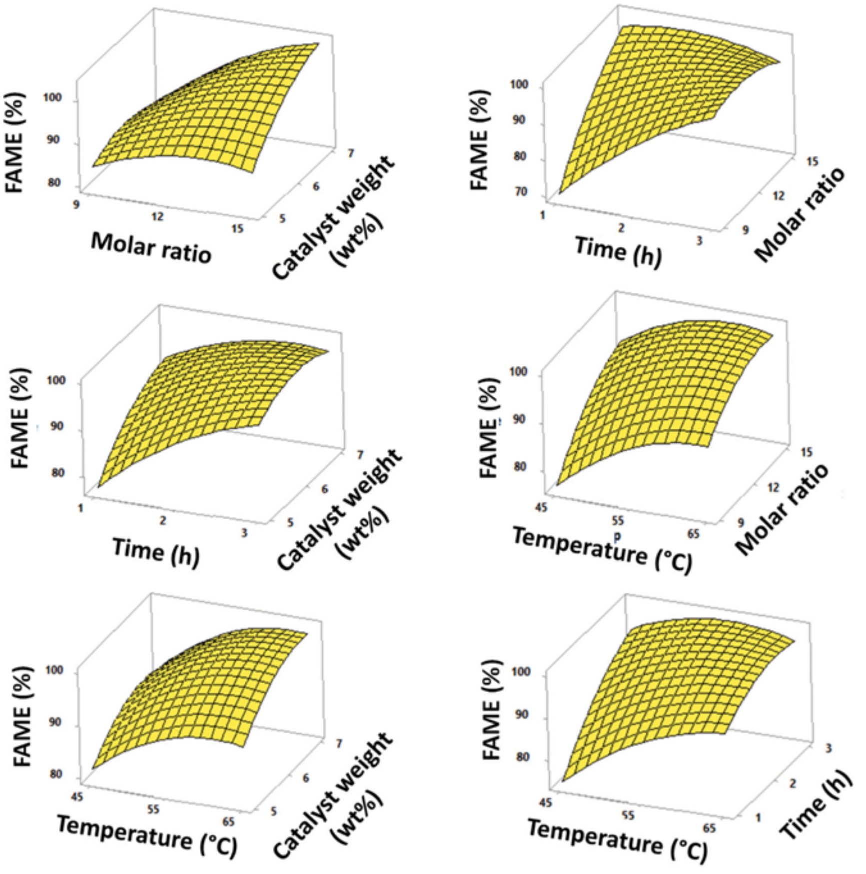

Fig. 5. The Surface plots showing the effects of different parameters on the biodiesel production over lithium silicate.

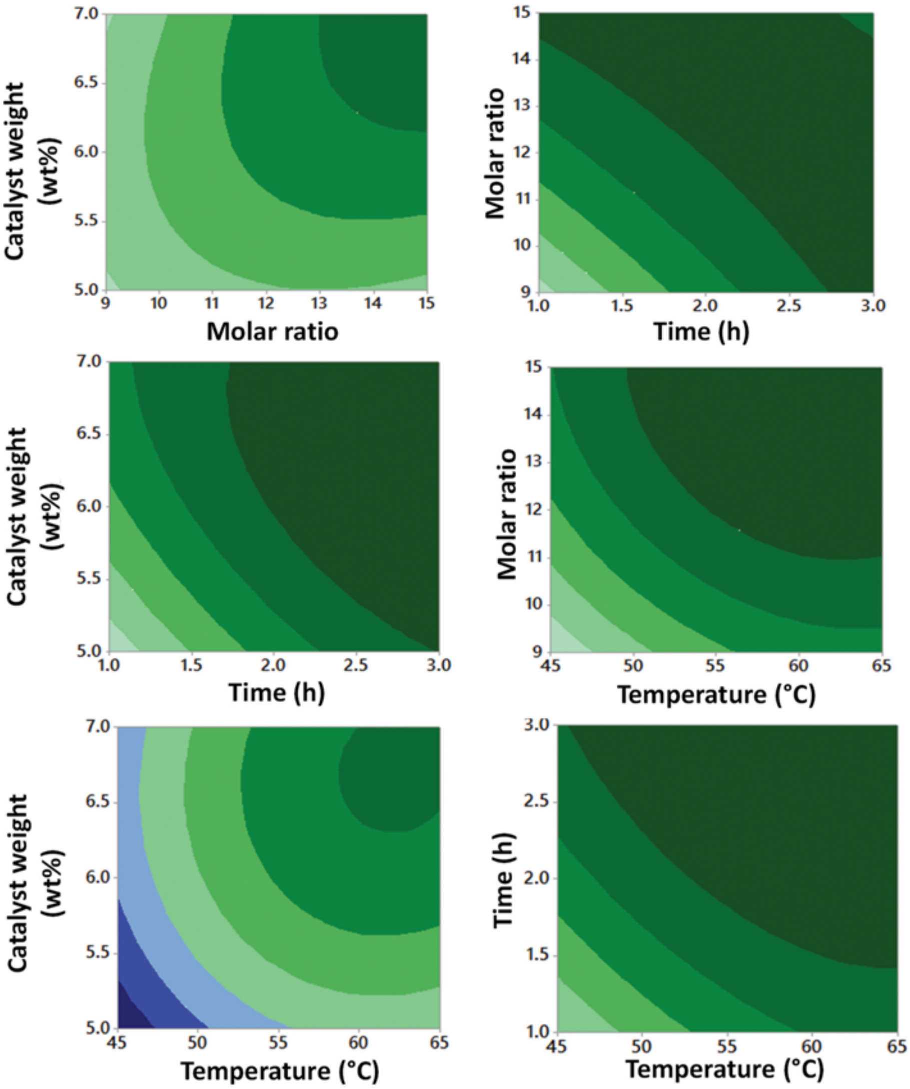

Fig. 6. Contour plots showing the distribution of FAME w.r.t different parameters.

5), which was given by the software Minitab. The linear, square and the interaction effects of the four different reaction parameters on the FAME content were given by the ANOVA table. The p-values and F-values of these parameters suggest the significance of the variables for this model. The lower P-values (<0.05) of the temperature, catalyst weight, methanol : oil molar ratio and reaction time indicates the significance of the model. Also, the model predicted an R^2 value of 82.4%, which suggests the suitability of the model for use in optimization of the lithium silicate catalyzed biodiesel production.

To evaluate the validity of the model, four random experimental trials as predicted by the software were performed (Table 6). In all these experiments, the expected and observed FAME values were in good agreement. The correlation coefficient was calculated as 0.95. Since the correlation coefficient is close to unity, the model is significant for the optimization of lithium silicate catalyzed biodiesel production. The optimum conditions predicted for the production of biodiesel are: reaction temperature 55 °C, methanol : oil molar ratio 15 : 1, catalyst weight 7 wt%, and reaction time 2.5 h.

Normally, the independent analysis of reaction parameters is difficult due to the interaction effects between the variables. The regression equation gives the interaction effect, which is graphically presented in the form of contour plots (Fig. 6). The distribution of FAME content with respect to different reaction parameters can be obtained in this case. The contour area gives the FAME content under the suggested experimental conditions. In all the contour plots, the relation between two different parameters is shown while the other parameters are kept at the medium values (a temperature of 55 °C, reaction time of 2 h, the methanol : oil molar ratio of 12 : 1 and a catalyst concentration of 6 wt%). The elliptical shape of the plots refers to the significance of the plotted parameters on the FAME content [64].

The response surface plots showing the effects of different parameters on the FAME content in the transesterification of waste cooking oil over lithium silicate are given in Fig. 5. It consists of a set of six different plots. In Fig. 5(a), the interaction effect of catalyst weight and molar ratio on the FAME content is depicted while the other two parameters, reaction time and reaction temperature

Table 5. Analysis of variance for the second order polynomial model for optimization of biodiesel production over lithium silicate

Source	DF	Adj SS	Adj MS	F-value	P-value
Model	14	1904.50	136.036	4.02	0.010
Linear	4	1392.38	348.095	10.28	0.001
Temp	1	314.68	314.675	9.29	0.010
Time	1	489.86	489.857	14.47	0.003
Mol ratio	1	417.37	417.366	12.33	0.004
Cat wt	1	170.48	170.479	5.04	0.044
Square	4	112.06	28.016	0.83	0.533
Temp*temp	1	73.94	73.937	2.18	0.165
Time*time	1	45.11	45.111	1.33	0.271
Mol ratio*mol ratio	1	54.98	54.984	1.62	0.227
Cat wt*cat wt	1	45.42	45.422	1.34	0.269
2-Way Interaction	6	400.06	66.676	1.97	0.150
Temp*time	1	49.98	49.985	1.48	0.248
Temp*mol ratio	1	12.29	12.285	0.36	0.558
Temp*cat wt	1	1.35	1.346	0.04	0.845
Time*mol ratio	1	243.52	243.516	7.19	0.020
Time*cat wt	1	36.00	36.000	1.06	0.323
Mol ratio*cat wt	1	56.93	56.927	1.68	0.219
Error		12	406.25	33.854	
Lack-of-fit	10	405.66	40.566	136.57	0.007
Pure error		2	0.59	0.297	
Total		26	2310.75		

were kept constant as same before, respectively. It is observed that the FAME content increases with increase in both catalyst weight and methanol:oil molar ratio. Also, it reaches a maximum value of 100% in the medium values of catalyst weight and oil : methanol molar ratio. In Fig. 5(b), the effects of reactant's molar ratio and reaction time on the FAME content are plotted. The FAME content increases with increase in reaction time; at lower reaction time of 1 h, the FAME content is only about 70%. This increases with time and at 3 h, maximum biodiesel conversion is obtained at which the lower oil : methanol molar ratio of 1 : 9 is suggested for the maximum conversion. Fig. 5(c) explains the effects of catalyst weight and reaction time on the FAME content. From the graph, the FAME content increases with increase in catalyst weight and reaction time. Fig. 5(d) represents the response surface plots to understand the influence of molar ratio and temperature on the FAME content. The increase in temperature had a positive effect in the transesterification reaction, which increased the biodiesel yield. The FAME content increased with increase in methanol : oil molar ratio. Fig. 5(e) explains the variation of FAME content with change in the catalyst weight and temperature. A mutual effect is observed for the two parameters on the FAME content. Increase in both catalyst weight and temperature increases the yield of biodiesel produced. Fig. 5(f) describes the impact of reaction time and temperature on the FAME content. The higher the reaction temperature, the higher will be the FAME content. Increase in reaction time also favors the FAME content.

The catalytic activity of the catalyst under the optimum reaction conditions suggested by the RSM technique was compared with the reported data over other heterogeneous catalysts, and the results are presented in Table 7. Also, the catalytic activity results of lithium based catalysts comparing the operating conditions, efficiency of the process, catalyst, is tabulated and given in Table 9. The lower reaction temperature and lower reaction time at reasonable metha-

Table 6. Validation experimental trials

Sl. no.	Temp. (°C)	Time (h)	Methanol/oil molar ratio	Catalyst weight (wt%)	Expected FAME (%)	Observed FAME (%)
1	55	2.5	15	7	99.27	100
2	45	2.5	12	6	91.78	90.05
3	50	2.5	15	6	95.80	96.43
4	60	2	9	6	89.73	91.06

Table 7. Comparison of the transesterification activity and the optimum reaction conditions given by RSM in the biodiesel production by different heterogeneous catalysts with the present work

Sl. no.	Catalyst system	FAME content/ Conversion/Yield (%)	Reaction conditions				References
			Methanol : oil molar ratio	Time (h)	Catalyst amount (wt%)	Temperature (°C)	
1	$Ca(NO_3)_2/Al_2O_3$	94	65 : 1	3	10	65	[65]
2	CaO-MgO mixed oxide	93.55	38.67 : 1	3.44	3.7	115.87	[66]
3	Sr/ZrO_2	79.7	29 : 1	1.27	2.7	115.5	[67]
4	Montmorillonite KSF	79.6	8 : 1	3	3	190	[68]
5	Sulfated zirconia	97.5	12 : 1	3	8	150	[69]
6	CaO/Al_2O_3	98.64	12.14 : 1	5	5.97	64.29	[70]
7	Na_2O/NaX	99.3	6 : 1	6	10	60	[71]
8	$Sr_3Al_2O_6$	95.7	25 : 1	1.1	1.3	60	[72]
9	Li_2SiO_3	100	15 : 1	2.5	7	55	Present work

Table 8. Fuel properties of biodiesel obtained under optimum reaction conditions* using lithium silicate as catalyst

Parameters	Methods	Unit	Limits	Standards	Biodiesel
*Ester content	EN14103	wt%	96.5 min	EN14214	100
*Free glycerol	EN14105	wt%	0.02 max	EN14214	0.00
*Monoglyceride	EN14105	wt%	0.8	EN14214	0.00
*Triglyceride	EN14105	wt%	0.20	EN14214	0.00
*Total glycerol	EN14105	wt%	0.25 max	EN14214	0.00
Acid value	EN14104	mg KOH/g	0.50 max	EN14214	0.10
Water content	EN ISO 12937	mg/kg	500 max	EN14214	0.00
Viscosity	D445	mm^2/s	1.96-6.0	ASTMD6751	3.82
Density	EN ISO 3675	g/m^3	860-900	EN14214	868

*15 : 1 methanol-to-oil molar ratio, 7 wt% catalyst, 55 °C reaction temperature and 2.5 h reaction time

Table 9. Lithium based catalysts for the transesterification reaction

Sl. no.	Catalyst	FAME yield/Content/ Conversion (%)	Optimum reaction conditions [Catalyst amount (wt%), methanol : oil molar ratio, reaction temperature (°C) reaction time (h)]	Reference
1	Li_2CO_3	97.2	12, 32 : 1, 65, 2	[28]
2	Lithium silicate	86.7	4, 24 : 1, 65, 3	[29]
3	Li_4SiO_4	98.8	1, 12 : 1, 65, 3	[30]
4	Lithium orthosilicate	98.1	6, 18 : 1, 65, 2	[31]
5	lithium silicate	96.6	3, 9 : 1, 65, 3	[32]
6	Cement	98.5	32.8, 24 : 1, 65, 3	[33]
7	$LiAlO_2$	97.5	6, 24 : 1, 65, 2	[34]
8	Li_2TiO_3	98.5	6, 24 : 1, 65, 2	[35]
9	Lithium silicate	99.04	6, 12 : 1, 62, 3	[36]
10	Lithium silicate	76.2	3, 18 : 1 68, 4	[37]

nol : oil molar ratio with high FAME content is the highlight of the present work compared to other studies reported for biodiesel production.

The fuel properties of the biodiesel prepared over lithium silicate catalyst under the predicted optimum reaction conditions were determined, and it was found that the biodiesel meets the standard specifications of ASTM D 6751 and EN 14214 (Table 8). Thus, the catalyst is found to be highly effective and is suitable for the industrial scale up.

3. Reusability Studies

After the reaction, under the optimum reaction conditions, the catalyst was recovered from the reaction mixture and washed several times with methanol. The catalyst was then dried at 90 °C, activated at 650 °C for 1 h, and reused for the biodiesel production. The catalyst was stable upto three cycles yielding a FAME content of 96.9% in the 3rd cycle and the catalytic activity was dropped to 86.8% at the 5th cycle (Fig. 7). The percentage composition of various reaction products formed during the transesterification reaction in repeated runs is given in Table S1 (supplementary information).

FTIR spectroscopy, XRD and TEM analyses of the catalyst after the third run were carried out to understand the nature and morphology of the catalyst after the repeated cycles of reaction. The catalyst structure remained unaltered even after the reuse, as it is evident from the FTIR spectrum of the reused sample after third cycle (Fig. 2). XRD patterns of fresh catalyst and the used catalyst are shown in Fig. 3. From Fig. 3, all the diffraction peaks corresponding to Li_2SiO_3 phase were retained in the reused catalyst. In the used catalyst, additional peaks of silica are observed and the

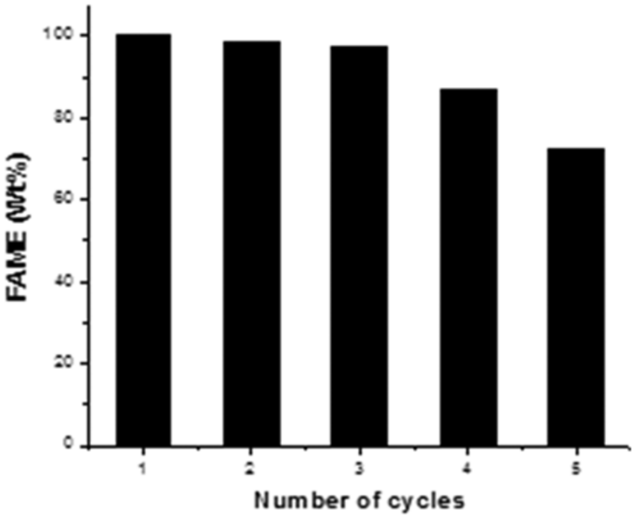

Fig. 7. Reusability results with the following reaction conditions: 15 : 1 methanol : oil molar ratio, 7 wt% catalyst, 55 °C reaction temperature and 2.5 h reaction time.

peak corresponding to $Li_2Si_2O_5$ phase disappeared, which may be due to the leaching of some amount of lithium during the repeated runs of reaction. The TEM and high resolution TEM image of the reused catalyst (Fig. 4(e) and 4(h) respectively) further confirms the retention of catalyst structure and porous morphology.

CONCLUSION

We have tested the applicability of the principles of Box Behnken design and response surface methodology for the optimization of different reaction parameters in the production of biodiesel using lithium silicate as the heterogeneous catalyst. 100% yield of biodiesel was obtained under the suggested optimum reaction conditions of methanol : oil molar ratio of 15 : 1, catalyst amount of 7 wt% of oil, reaction temperature of 55 °C and reaction time of 2.5 h, model predicted a conversion of 99.27%. The methyl ester products obtained under the optimized mild reaction conditions were analyzed, and it is confirmed that the fuel properties met the specification of biodiesel as mentioned in international standards, indicating its applicability as a diesel fuel substitute. The catalyst was found to be effectively reusable, leading to the formation of fuel grade biodiesel at a low reaction temperature of 55 °C till three repeated cycles.

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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Supporting Information

Statistical optimization for lithium silicate catalyzed production of biodiesel from waste cooking oil

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EXPERIMENTAL SECTION

S1. Degumming of Oil

Waste cooking oil is first heated to 60 °C. As the temperature is achieved, 0.01% phosphoric acid by weight of oil is added to it. The resultant mixture is then stirred for 30 minutes. Then, 2% water is added to the oil and is then heated to 70-80 °C for 15 minutes. Gums present in the oil will settle down and then the oil is dried using anhydrous sodium sulphate.

S2. Pretreatment of Oil

The degummed oil is then subjected to pre-treatment in a round bottom flask using methanol and an acid. A 1 : 6 molar methanol and 6% Con. HCl by weight of the oil is mixed and this mixture is added to the oil and is stirred for 1 h at 65 °C. After that the reaction mixture is kept for separation of the two layers. Lower oil layer is taken and washed several times with water to make it acid free. Then, the pretreated oil is dried over anhydrous sodium sulphate.

S3. Preparation of Biodiesel Sample for GC Analysis

100 mg of biodiesel sample was weighed in a sample bottle and 100 μL derivatisation reagent (MSTFA) is added to it using a micro syringe. The sample is slowly shaken for 10 min for proper derivatisation and allowed to stand for 20 min at room temperature to allow the derivatisation reaction to complete. Following derivatisation, 8 ml heptane is added and the vial is capped and shaken. Now, the sample is ready for the analysis. Then, 1 μL solution is withdrawn and is injected into GC using the micro syringe. From the gas chromatogram obtained, the FAME content of biodiesel and the yields of other products can be determined by comparison with standards.

Table S1. Percentage composition of various reaction products formed during the transesterification reaction in repeated runs

Sl. no.	Number of runs	[*]Reaction products (%)			
		FAME content (%)	Monoglyceride (%)	Diglyceride (%)	Unreacted oil (%)
1	1	100	0.0	0.0	0.0
2	2	98.7	0.32	0.41	0.57
3	3	96.9	0.435	0.4549	2.2101
4	4	86.8	0.559	0.2087	12.4323
5	5	72.1	0.0857	0.1345	27.6798

[*] 15 : 1 methanol : oil molar ratio, 7 wt% catalyst, 55 °C reaction temperature and 2.5 h reaction time