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Synthesis of Biodiesel from Canola Oil Using Heterogeneous Base Catalyst

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Abstract A series of alkali metal (Li, Na, K) promoted alkali earth oxides (CaO, BaO, MgO), as well as K_2CO_3 supported on alumina (Al_2O_3), were prepared and used as catalysts for transesterification of canola oil with methanol. Four catalysts such as K_2CO_3/Al_2O_3 and alkali metal (Li, Na, K) promoted BaO were effective for transesterification with >85 wt% of methyl esters. ICP-MS analysis revealed that leaching of barium in ester phase was too high ($\sim$1,000 ppm) when BaO based catalysts were used. As barium is highly toxic, these catalysts were not used further for transesterification of canola oil. Optimization of reaction conditions such as molar ratio of alcohol to oil (6:1–12:1), reaction temperature (40–60 °C) and catalyst loading (1–3 wt%) was performed for most efficient and environmentally friendly K_2CO_3/Al_2O_3 catalyst to maximize ester yield using response surface methodology (RSM). The RSM suggested that a molar ratio of alcohol to oil 11.48:1, a reaction temperature of 60 °C, and catalyst loading 3.16 wt% were optimum for the production of ester from canola oil. The predicted value of ester yield was 96.3 wt% in 2 h, which was in agreement with the experimental results within 1.28%.

Keywords Biodiesel · Canola oil · Solid base catalyst

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Introduction

A solid base is a promising alternative to a homogeneous base catalyst for biodiesel production. Use of a solid base in biodiesel production offers several process advantages including elimination of a quenching step to isolate products, thus reducing the risk of contaminated water, and the opportunity to operate a continuous process [1]. Use of solid base for transesterification of vegetable oils has been reported in the literature [1–4]. Alkali earth oxides and hydroxides have potential as solid bases for transesterification [5]. The origin of basic sites in alkali earth oxides has been generated by the presence of M^{2+} and O^{2-} ion pairs in different co-ordination environments [6]. The basic strength of group II oxides and hydroxides increase in the order Mg < Ca < Sr < Ba [1].

Catalytic activities of calcium oxide, methoxide, barium hydroxide and sodium hydroxide were compared for transesterification of rapeseed oil [5]. Calcium compounds are cheaper and less toxic but due to the low solubility of these compounds in methanol they are less active than sodium hydroxide. Barium hydroxide is a strong base but the strong toxicity and high methanol solubility of the barium hydroxide makes it an environmentally unfriendly catalyst for biodiesel production.

Attempts have been made to promote the basicity of the alkali earth oxides by doping with an alkali metal such as lithium (Li) [1]. An increase in the number of basic sites of alkali earth oxides was believed to occur via exchange of lattice M^{2+} for M^+ upon calcinations leading to the formation of O^- vacancies. Li-promoted CaO catalysts with Li loadings in the range of 0.26–4.0 wt% have been used for transesterification of glyceryl tributyrate and methanol. A Li content of 1.23 wt% gave the optimum activity towards the transesterification with 100% conversion in 20 min.

The K_2CO_3/Al_2O_3 catalyst is very well known to catalyze many organic reactions such as isomerisation, alkylation [7]. Also the alkali metal salt loaded alumina (Al_2O_3) is an efficient solid base catalyst for transesterification [4]. The catalyst showed high activity in the presence of a large amount of water. Selective transesterification of triolein with methanol using alumina loaded with alkali metal salt has been reported. K_2CO_3 loaded on alumina gave the highest yields, namely 94% methyl oleate at 60 °C in 1 h.

Activity of alkali metal loaded alkali earth oxide and alumina as a catalyst for the transesterification reaction is reported only for model compounds such as triolein and tributyrate; however, the use of these catalysts for the biodiesel production using real feedstock such as vegetable oil has not been reported so far. Activity of the solid base catalyst for the transesterification of vegetable oil, which is a real feedstock for biodiesel production is quite important.

The catalytic activity of the Li doped CaO was investigated for the transesterification reaction [1], whereas the activities of the catalysts prepared from other cheap alkali metals such as Na and K doped on different earth oxides (MgO, BaO) has not been reported. Comparison with the oxides as such is normally expected to measure the effect of metal exchange.

The aim of the present work was to screen various solid bases for the transesterification of canola oil and to perform the process optimization for the most efficient and environmentally friendly catalyst to maximize the ester yield. Ten solid bases including Li, Na, and K doped CaO, BaO and MgO and K_2CO_3 supported on alumina were prepared in the present work. Leaching of the catalysts in the ester phase was measured using ICP-MS analysis. Optimization of the reaction conditions such as molar ratio of oil to alcohol, reaction temperature and catalyst concentration for the most efficient and environmentally friendly catalyst was performed using the response surface methodology.

Materials and Methods

Materials

CaO, MgO and KNO_3 (99%) were purchased from Fisher Scientific, New Jersey, USA. BaO (97%), $LiNO_3$ (99.9%) and Methanol (99.8%) used in the present study were obtained from Sigma–Aldrich, Missouri, USA. $NaNO_3$ (99%), K_2CO_3 (AR grade) and γ-alumina were purchased from BDH Inc., Toronto, ON and SUD-CHEMIE India Ltd, Delhi, India, respectively. Canola oil was purchased from local grocery shop.

Catalyst Preparation and Characterization

The alkali metal (Li, Na and K) doped CaO, BaO and MgO were prepared by the wet impregnation of the corresponding nitrates on the support with a theoretical metal content of 1.25 wt% on alkali earth oxide as per the method given by Watkins et al. [1]. A K_2CO_3-loaded alumina catalyst was prepared by the wet impregnation method as given by Ebiura et al. [4]. K_2CO_3 was loaded at a dose of 2.6 mmol/γ-Al_2O_3 as metal.

The strength of the basic sites in prepared catalysts was compared using temperature programmed desorption (TPD) of CO_2 in a CHEM BET-3000 (Quanta Chrome, USA) instrument. About 0.05 g of powdered sample was taken in a quartz "U" tube and degassed at 120 °C for 1 h with helium at a flow rate of 35 ml/min. The sample was then cooled to 40 °C and then 3% v/v of CO_2 in nitrogen (Praxair, Toronto, ON) gas was passed though the sample for 30 min. While heating, the helium flow of 35 ml/min was then started though the sample. The CO_2 desorption from the sample was recorded using a thermal conductivity detector (TCD) at a rate of 10 °C/min up to 850°C.

Transesterification of Canola Oil

The transesterification of canola oil with methanol was carried out with all the ten catalysts in the particle size range of 0.25–1.5 mm under identical operating conditions and their activities were compared. In all the cases, the reaction was carried out in an Erlenmeyer flask at 50 °C for 4 h using 50 g of canola oil, a 6:1 alcohol to oil molar ratio, 2 wt% catalyst loading at constant stirring speed. The catalyst was preheated at 100 °C before adding it to the reaction mixture.

The optimization study for the various reaction conditions such as temperature (40–60 °C), molar ratio of alcohol to oil (6:1–12:1) and catalyst loading (2–4 wt%) was conducted in a 500 ml Parr reactor (Parr Instrument Co. Illinois, USA). Initially, the reactor was charged with 100 g of oil and heated up to the desired temperature with optimized stirring speed of 600 rpm. Catalyst was preheated at 100 °C before adding to the reaction mixture. Methanol and catalyst were added to the pre-heated oil. The reaction was continued for 2 h.

Analysis of the Ester Phase

The conversion of canola oil to methyl ester was measured by the GPC method consisting of a HPLC pump (Agilent HPLC 1100 series, Mississauga, Canada), refractive index (RI) detector, an autosampler and chemstation software.

Two 300 × 7.8 mm Phenogel columns of 5 μm and 100-Å pore size (Phenomenex, Torrance, CA, USA) were connected in series and protected by a guard column of 50 × 7.8 mm and 10 μm particle size. HPLC grade tetrahydrofuran was used as a mobile phase. The reaction was monitored by calculating the percentage ester yield and oil conversion using Eqs. 1, 2. The leaching of the metal in the ester phase after the separation of liquid by simple filtration was analysed using Perkin Elmer Elan 5000 ICP-MS instrument.

$$\text{Ester yield(wt\%)} = ((\text{wt. of methyl esters in the product}) / (\text{wt. of ester phase})) \times 100 \quad (1)$$

$$\text{Oil conversion(wt\%)} = ((\text{triglyceride conc. in the product}) / (\text{initial triglyceride conc.})) \times 100 \quad (2)$$

Process Optimization

A 3-factor, 2-level Central Composite Design (CCD) was used to design the experiments for process optimization studies. A total of 20 experiments were performed in random order with six center points. The parameters selected for the study of transesterification of canola oil were: a temperature of 40–60 °C; a catalyst loading of 2–4 wt%; and a molar ratio of 6:1–12:1 (MeOH:oil).

Results and Discussion

Basicity of Prepared Catalyst

The strength of basic sites of prepared catalysts was analyzed by temperature programmed desorption (TPD) of CO_2. The amounts of CO_2 chemisorbed and the desorption profiles for each sample were recorded using TCD. The TPD profiles of the prepared catalysts (Fig. 1) clearly indicate that CO_2 desorbs at higher temperature (~ 700 °C) in case of alkali metal (Li, Na, and K) promoted BaO and K_2CO_3 doped Al_2O_3 catalyst in comparison to that of 450–650 °C in the case of the other catalysts under study. This indicates that the strengths of basic sites in these four catalysts were very high inspite of a fewer number of basic active sites (due to a low peak area) in comparison to other catalysts. Figure 1 also shows that the CaO-based catalyst contains some weak basic sites in addition to strong basic sites; however, the BaO-based catalyst contains only strong basic sites. The alkali metal promoted MgO catalysts were weakly basic. The relative peak areas of CO_2 desorbed from Li/MgO, Li/CaO and Li/BaO catalysts are 1.00:1.16:1.34 indicating that MgO-containing catalysts

are less basic than CaO and BaO supported catalysts. This trend is in accordance with the theoretical basicity of the group II metals that the basic strength of group II oxides and hydroxides increase in the order Mg < Ca < Sr < Ba. The basicity of Li doped alkali earth oxide was similar but not almost the same as Na or K doped alkali earth oxide. The relative peak areas of CO_2 desorbed from Li, Na and K doped CaO catalysts are 1:1.03:1.04. The effect of cation size of alkali metal on the alkaline oxides is minimal towards the basicity of the materials.

Screening of the Catalyst

The activity of the prepared catalysts, having different basic strengths towards the transesterification of canola oil with methanol, was measured in terms of methyl esters yield. The yield was defined as percentage ester present in the purified ester phase consisting of tri-, di-, mono-glyceride and ester.

Table 1 shows BET surface areas and the average pore diameter of the short-listed catalysts. The surface areas values were very low for the alkali metal-impregnated BaO catalyst; however, K_2CO_3/Al_2O_3 showed a fairly high surface area (118 m^2/g). All these catalysts appear to be meso-porous materials. The Li, Na and K contents in the fresh catalysts were ~ 1.25 wt% and also in K_2CO_3/Al_2O_3 the metal content is same as the theoretical (2.26 mol%) as determined by ICP-MS. Table 1 also shows the yield of methyl esters produced after transesterification of canola oil for 4 h under identical reaction conditions. The most active catalysts were found to be alkali metal (Li, Na, K) impregnated BaO catalysts (~ 96 wt% ester) and K_2CO_3 doped alumina catalyst (~ 85 wt% ester), which had the highest basic strength as mentioned above. Thus, it is clear that the basicity of the catalyst is responsible for its activity toward the transesterification and not the surface area or average pore diameter. The only other catalyst that showed significant activity towards the transesterification of canola oil was the Li/CaO catalyst (~ 71 wt% ester); however, the ester yield obtained using this catalyst was less than those of using alkali metal promoted BaO and K_2CO_3/Al_2O_3 catalyst. Hence, four catalysts such as Li/BaO, Na/BaO, K/BaO and K_2CO_3/Al_2O_3 were found promising with high activity towards the transesterification of canola oil.

The leaching of all these four efficient catalysts in the ester phase was measured using ICP-MS (Table 2). It was quite interesting to note that approximately 1,000 ppm barium was leached in the ester phase; however, leaching of the impregnated metal was quite low at the end of the reaction. Unfortunately, soluble barium compounds are

Fig. 1 TPD profile of catalysts
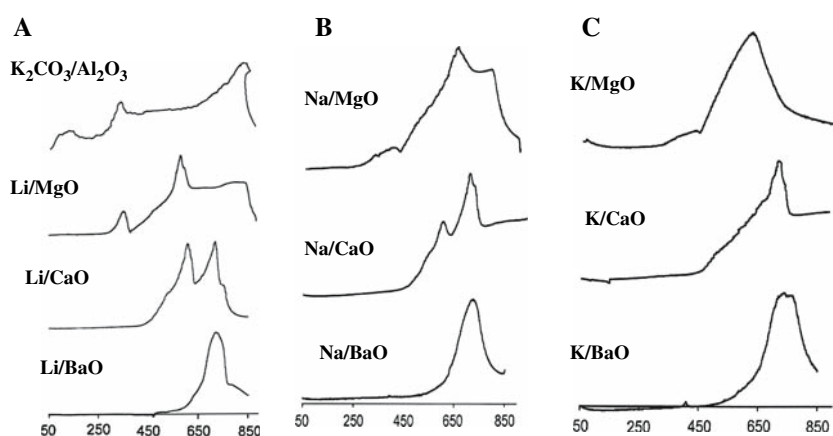
highly toxic in nature and can create serious environmental and health problems when biodiesel from canola oil, using barium based catalyst, is used as a diesel fuel extender. Metal content in commercial summer and winter diesel was also measured and compared with those present in biodiesel prepared by using these four catalysts. Surprisingly, summer and winter diesel showed almost 35 ppm of Ca. We also carried out the reproducibility runs of these samples and the results were almost the same with only a ±1% error. It was observed that the metal content in commercial diesel fuel was very low compared to those in methyl esters obtained by the above process (Table 2). Therefore, alkali metal-impregnated BaO cannot serve as environmental friendly heterogeneous catalyst for biodiesel preparation. Based on the activity towards transesterification and environmentally benign nature of the catalyst, K_2CO_3/Al_2O_3 was chosen for the optimization of the reaction conditions.

Process Optimization

The experimental data were analyzed by response surface methodology (RSM) for optimization of experimental variables. A second-order polynomial equation was generated as given below to fit the experimental data.

Ester produced (wt%)

$$= -73.6 + 2.5 \times A + 24.9 \times B + 8.8 \times C - 0.01 \\ \times A^2 - 1.29 \times B^2 - 0.39 \times C^2 - 0.26 \times A \times B \tag{3}$$

where A: temperature in °C, B: catalyst loading in wt% and C: molar ratio of alcohol to oil.

The statistical analysis for the tests performed on the model to prove its adequacy is shown in Table 3. It is quite evident from this table that Eq. 3 representing the model was significant (significance level probability less than 0.0001). The model terms (A, B, C and AB) in the equation were also significant as the probabilities of these terms was less than 0.05. The interaction effects of temperature with molar ratio as well as catalyst loading with molar ratio were insignificant, and these terms were removed from the model manually. The insignificant "Lack-of-fit" revealed that the proposed model fits well with the experimental

Table 1 Activity of various solid bases toward transesterification and their characteristics

Catalyst	BET surface area (m²/g)	Average pore diameter (Å)	Ester yield (wt%)
Li/CaO	–[a]	–[a]	70.7
Na/CaO	–	–	6.0
K/CaO	–	–	6.5
Li/MgO	–	–	3.8
Na/MgO	–	–	2.6
K/MgO	–	–	2.6
Li/BaO	4.0	66.4	96.7
Na/BaO	3.8	66.4	97.5
K/BaO	6.1	50.2	96.9
K_2CO_3/Al_2O_3	118.0	130.2	84.6

Reaction conditions: molar ratio of oil to alcohol 1:6; catalyst loading, 2 wt%; temperature, 50 °C; reaction time, 4 h

[a] Not determined

Table 2 Metal content in ester and diesel fuel

Sample	Metal (ppm)					
	Li	Na	Ca	Ba	Al	Mg
Na/BaO[a]	–	–	–	1050.4	–	–
Li/BaO[a]	14.14	–	–	882.7	–	–
K/BaO[a]	–	–	–	944.3	–	–
Summer diesel	–	–	38.3	0.1	–	1.20
Winter diesel	0.42	–	36.8	–	–	2.4

[a] Ester obtained by using Na/BaO, Li/BaO, K/BaO as a catalyst

Table 3 Summary of statistical analysis

Source	Degree of freedom	Sum of squares	Prob > F	
Model	7	916.35	<0.0001	Significant
Temperature (A)	1	293.82	<0.0001	
Catalyst loading (B)	1	222.53	<0.0001	
Molar ratio (C)	1	220.21	<0.0001	
Temperature^2 (A^2)	1	18.49	0.0006	
Catalyst loading^2 (B^2)	1	19.75	0.0005	
Molar ratio^2 (C^2)	1	47.49	<0.0001	
Temperature × Catalyst loading (AB)	1	55.14	<0.0001	
Lack of Fit	5	4.25	0.4014	Not significant
R-squared			0.99	
Adj R-squared			0.99	
Pred R-squared			0.97	
Adeq precision			47.82	

data. The Adjusted and Predicted R-Squared values were in reasonable agreement, which also re-confirmed that the data fits well with the model. Adequate Precision is a measure of signal to noise ratio. As per the requirement of the model this ratio should be greater than four in order to show that the noise is not contributing any error in the response surface. In the present model, this value was 47.82, which is much higher than the requirement of the model, which showed that model didn't have any significant error due to noise.

The response surface plots showing the effect of molar ratio, temperature, and catalyst loading and their interactions on methyl ester yield are shown in Figs. 2–4. Figure 2 shows the effect of molar ratio and temperature and their mutual interaction on ester yield. It can be seen

that with increase in temperature, the ester yield increased linearly. However, there was no significant effect on ester yield when the molar ratio was increased beyond 10:1. The effect of catalyst loading and molar ratio on the ester yield was also studied (Fig. 3). Catalyst loading showed linear effect on ester yield whereas molar ratio showed curvilinear surface, which indicated that beyond a certain molar ratio (10:1) the ester yield didn't change significantly. Figure 4 shows the effect of temperature and catalyst loading on ester yield. As observed in Figs. 2 and 3, both of the parameters showed a linear trend i.e., there was a significant change in the ester yield with an either increase or decrease in these parameters and therefore their interaction was modeled in the second order polynomial as shown by Eq. 3.
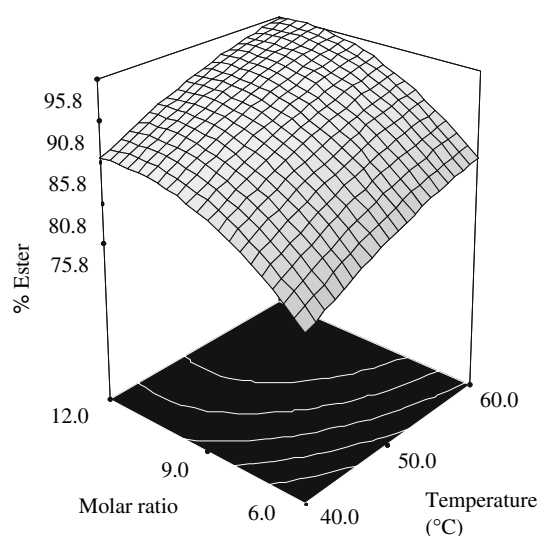
Fig. 2 Response surface plot of molar ratio and temperature as a function of ester yield
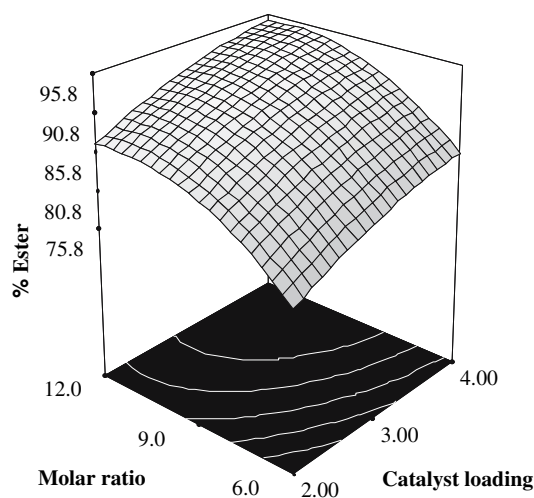
Fig. 3 Response surface plot of molar ratio and catalyst loading as a function of ester yield
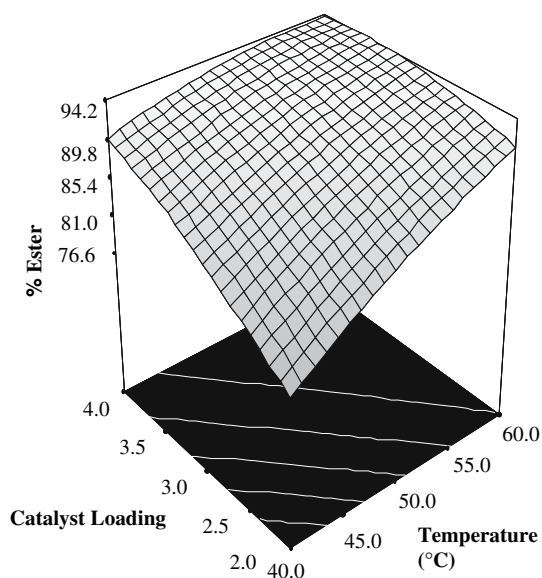
Fig. 4 Response surface plot of catalyst loading and temperature as a function of ester yield
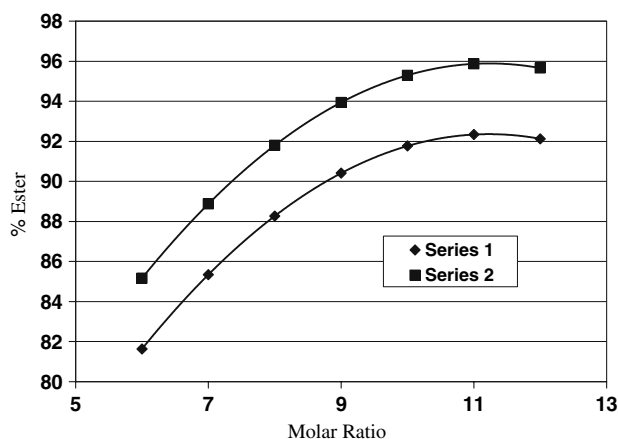
Fig. 5 Plot of percentage ester against molar ratio at mid and extreme range of experimental conditions. *Series 1* temperature 50 °C, catalyst loading 3 wt%. *Series 2* temperature 60 °C, catalyst loading 4 wt%

A perturbation plot (not shown) gives a 2-D view of the behaviour of all the variables within the design space showed that the effect of molar ratio on % ester showed a curvilinear trend whereas temperature and catalyst loading showed a linear trend. This indicated that the temperature and catalyst loading have a significant effect on ester yield whereas an increase in the molar ratio beyond 10:1 did not affect the ester yield significantly. The curvilinear trend of the effect of the molar ratio on ester yield was reconfirmed by plotting % ester against molar ratios (Fig. 5) at the mid and high range of experimental data points. This figure also showed the curvilinear trend (plateau) at high molar ratios, which revealed that when the molar ratio was increased

from 10:1 to 12:1 the change in ester yield was not significant even at the mid and high ranges of experimental conditions.

Attaining Optimum Conditions and Model Verification

Numeric optimization was used to optimize the ester yield and keep the other variables in range of the experimental values. The suggested optimum ester yield was 96.3 wt% in 2 h at 60 °C, 3.16 wt% catalyst loading and 11.48:1 molar ratio of alcohol to oil with a desirability of 0.997. The validity of the predicted model was examined by performing the experiment at these optimum synthesis conditions. The ester yield was 94.2 wt%, which showed a deviation of 1.28% from the predicted value.

Recently a paper published on the transesterification of soybean oil catalyzed by KNO_3/Al_2O_3 as a solid base indicated 87% oil conversion when the reaction was carried out at reflux of methanol, using amolar ratio of methanol to soybean oil of 15:1, a reaction time of 7 h, and a catalyst amount of 6.5% [8]. Xie et al. [8] reported percentage oil conversion, which is higher than % ester yield. Hence, % ester yield obtained by using KNO_3/Al_2O_3 catalyzed transesterification of soybean oil would be much less. The activity of the K_2CO_3/Al_2O_3 is much higher compared to that of KNO_3/Al_2O_3 catalyst at their optimum operating conditions, indicating that K_2CO_3/Al_2O_3 may be an efficient and environmentally friendly solid base for the transesterification of canola oil. The potassium content in the biodiesel was measured by flame photometer, which indicated that it leaches by 1,900 ppm into the biodiesel fuel. The catalyst modification is recommended in order to prevent potassium leaching into the fuel.

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