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Transesterification of Camelina Sativa Oil Using Heterogeneous Metal Oxide Catalysts

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Received April 23, 2009. Revised Manuscript Received June 26, 2009

Camelina sativa oil provides a reliable solution for biodiesel production by providing a sustainable, low-input biofuel feedstock option in some climates. In the present study, optimization of the transesterification of camelina sativa oil using different heterogeneous metal oxide catalysts, i.e., BaO, SrO, MgO, and CaO, was evaluated. The results of comparative experiments showed that the most effective catalyst was 1 wt % BaO, which showed an >80% yield of camelina to biodiesel conversion in 3 h at 100 °C. The relative order of the effectiveness of the catalysts was BaO > SrO > CaO > MgO. These catalysts were characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM), and Brunauer–Emmett–Teller (BET) to obtain their physical and chemical properties. The important variables affecting the methyl ester yield during the transesterification reaction are the molar ratio of alcohol/oil, catalyst amount, and reaction temperature. The fuel properties of biodiesel produced were compared to American Society for Testing and Materials (ASTM) standards for biodiesel.

1. Introduction

Biodiesel is a fuel comprised of monoalkyl esters of long-chain fatty acids derived from renewable feed stocks, such as vegetable oils or animal fats. In recent years, because of global warming, environmental pollution, and depletion of fossil resources, biodiesel has gained more and more attention as a promising alternative fuel. Biodiesel is a nontoxic, biodegradable, renewable, and environmentally friendly fuel.^{1–3} In addition, biodiesel is better than regular diesel fuel in terms of sulfur content, flash point, aromatic content, and cetane number.⁴

Vegetable oils can be a promising alternative to regular diesel fuel because they are renewable in nature and can be produced locally and environmentally friendly as well. Under this category, camelina sativa is an underexploited crop species of great economical potential. Camelina sativa oil is rich in Omega-3 fatty acids and has an average yield of 1200–1400 pounds per acre.⁵ The cold-pressed and filtered camelina sativa oil has an increased maximum power output for the seed oil of 43.25 kW as compared to 38.50 kW for the mineral fuel.⁶ The production cost for camelina sativa oil is substantially lower than many other oil crops, such as rapeseed, corn, and soybean, which makes camelina an attractive potential crop for biodiesel production and many other industrial

applications.⁷ Camelina sativa has a positive energy balance for the production of biodiesel ester (net energy ratio of 1.47).⁸ In a single-stage laboratory esterification, the maximum yield of methyl ester can be obtained at room temperature from camelina sativa oil using KOH as a catalyst.⁹

In transesterification, the selection of the catalyst depends upon the amount of free fatty acid (FFA) present in the source oil. If the oil contains higher amounts of FFA, a two-step transesterification (acid esterification followed alkali transesterification) process is better suited.^{10,11} However, the reaction rate is slow, and higher molar ratios of methanol/oil are required to drive the reaction toward completion.¹ If the oil contains FFA less than 1 wt %, an alkali-catalyzed reaction is preferred for higher yield.³ Transesterification of vegetable oils can be carried out using both homogeneous (acid or base) and heterogeneous (acid, base, and enzymatic) catalysts.^{12,13} Homogeneous base catalysts provide much faster reaction rates than heterogeneous catalysts in the transesterification of oils. However, the catalysts dissolve fully in the glycerin layer and partially in the biodiesel, which makes the product separation and purification difficult.^{2,14,15} Heterogeneous catalysts, on the other hand, make product separation easier and leave catalysts reusable,¹⁶ reducing environmental impact and process cost. Many types of acid heterogeneous catalysts have been reported for biodiesel production, such as sulfated

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metal oxides, sulphonated amorphous carbon, and ion-exchange resin.^{17–19} However, acid catalysis requires a high reaction temperature and long reaction time and shows weak catalytic activity. On the other hand, basic heterogeneous catalysts, for example, metal oxides and zeolites, exhibit high catalytic activity in transforming oil into ester.^{20,21} Transesterification of soybean oil using different heterogeneous metal oxide catalysts (MgO, PbO, PbO₂, and Ti₂O₃) was studied at different temperatures and high pressure.¹⁶ Zinc oxide (ZnO) loaded with lithium was demonstrated to be an effective catalyst for the transesterification of soybean oil with methanol.²² With the supported CaO/MgO catalyst, the conversion of rapeseed oil reached 92% at 64.5 °C.²³ Transesterification of sunflower oil was carried out with calcium oxide (CaO) in supercritical methanol.²⁴ The kinetics study of the transesterification of soybean oil using metal oxide catalysts in a high-pressure–high-temperature reactor at 225 °C produced a maximum biodiesel yield of 85%, obtained with BaO as a catalyst in 14 min.¹⁶ The yield of biodiesel obtained with SrO as a catalyst was >95% at a temperature below 70 °C with a reaction time of 30 min.²⁵

Extensive work has been performed on the transesterification of non-edible and edible vegetable oils using homogeneous and heterogeneous catalysts; however, no significant work has been performed on the optimization, oil characterization, or fuel analysis of camelina sativa oil using heterogeneous metal oxide catalysts. In the present work, a biodiesel optimization study for the camelina sativa oil using heterogeneous metal oxide catalysts (i.e., BaO, SrO, CaO, and MgO) has been carried out in detail.

2. Experimental Section

2.1. Materials and Methods. Cold-pressed camelina sativa oil was obtained from Marx Foods Company, NJ. Heterogeneous metal oxide catalysts, i.e., SrO, CaO, MgO, and BaO, were purchased from Alfa Aesar. To test the physio-chemical properties of the oil, ethanol (95%, v/v), potassium hydroxide flakes (KOH), hydrochloric acid, and diethyl ether were available from Fisher Scientific. Extra pure 99% methanol was purchased from Acros Organics. For GC–MS analysis, American Society for Testing and Materials (ASTM) D 6584 individual stock and internal standard mix kit (44898U, Supelco) was procured from Sigma-Aldrich. A round-bottom flask equipped with a water-cooled reflux condenser arrangement was used as a laboratory-scale reactor, and a hot plate with a magnetic stirrer was used for heating the mixture in the flask. For transesterification of the oils, the mixture was stirred at the same agitation speed of 1000 rpm for all test runs.

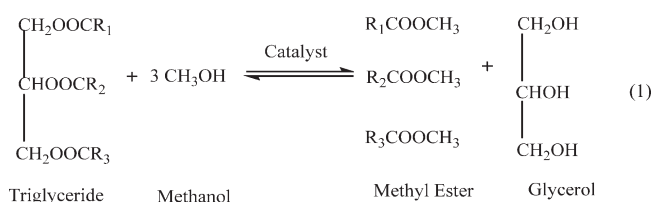
2.2. Characteristics of Camelina Sativa Oil and Catalyst. The quality of oil is expressed in terms of the physicochemical properties, such as acid value and saponification value. The saponification value of camelina oil was reported as 193.3 (mg of KOH/g). The acid value of camelina oil was found as 3.2 mg of KOH/g, corresponding to a FFA level of 1.58%. It has been reported that transesterification would not occur if the FFA content in the oil were above 3 wt %.²⁶

The viscosity at 40 °C and pour point of camelina sativa oil were determined as 14.0 mm²/s and –23.33 °C, respectively.

Textural characteristics of the catalysts, including multipoint Brunauer–Emmett–Teller (BET) surface area, Bopp–Jancso–Heinzinger (BJH) pore volume, and pore width, allowed the users to monitor the activity and stability of the catalysts. Textural characteristics were determined by N₂ adsorption–desorption at –196 °C in a Micromeritics ASAP 2020. Before the analysis, the samples were degassed under vacuum overnight at 450 °C.

X-ray powder diffractograms were recorded in a Rigaku Miniflex II X-ray diffractometer equipped with a graphite monochromator using Cu Kα radiation, 30 kV and 15 mA, to identify the crystalline structure present in the samples. For all samples, scattering intensities were measured over the angular range of 3° < 2θ < 75°, with a scan speed of 3° per min. The morphology and composition of the catalyst coated onto carbon paper were examined by scanning electron microscopy (SEM, HITACHI S-3400 N) equipped with energy-dispersive X-ray spectroscopy (EDS). To avoid charging effects, a very thin layer of palladium (Pd) was deposited onto the samples using the Denton Vacuum Desk II Sputtering unit.

2.3. Transesterification of Oil. For a successful reaction, the oil must be heated above 100 °C for 1 h to remove the water and other impurities as part of pretreatment. The FFA content in the oil was determined by a standard titrimetry method.²⁷ The transesterification reaction is represented by eq 1.



The experimental plan involved five methanol/oil ratios varying from 3:1 to 15:1; five catalyst concentrations, 0.25, 0.5, 1, 1.5, and 2 (% w/w, oil); five sets of reaction times, 0.5, 1, 1.5, 2, and 3 h; and five different reaction temperatures, 40, 60, 80, 100, and 130 °C.

In transesterification, 15 mL of oil from the pretreatment procedure was allowed to cool at normal temperature. Meanwhile, 1 wt % of BaO catalyst was dissolved in 7.5 mL of methanol, and the mixture was stirred for 10 min to ensure the complete mixing as part of catalyst activation.²⁸ Then, the catalyst–methanol mixture was poured into a 250 mL glass reactor containing pretreated oil and maintained at a reaction temperature of 100 °C for 3 h. At the end of the reaction, the reaction mixture was allowed to separate into two layers. The lower layer, which contained catalyst and glycerol, was drawn off. The crude methyl ester remained in the upper layer. The excess methanol in the ester phase was distilled off under a vacuum. Hot distilled water was sprayed over the surface of the ester and stirred gently to remove the entrained impurities and the glycerol. Washing was performed 2–3 times to remove all dissolved catalyst and glycerin in the ester layer. The lower layer was discarded, and a yellow-colored layer (biodiesel) was separated and then dried using sodium sulfate.

2.4. Analysis of Conversion of Biodiesel. For the quantification of reaction products, the samples were analyzed by a gas chromatography–mass spectrometry (GC–MS) system incorporated with an Agilent 5973N mass-selective detector (MSD) and an Agilent 6890 gas chromatograph equipped with a capillary column (HP-5 MS, 5% phenyl methyl siloxane, 30 m × 250 μm × 0.25 μm, nominal). Helium was used as the carrier gas. The injection was performed in splitless mode. The oven temperature program consists of the following steps: start at 50 °C (2 min) and ramp at 10 °C/min to 300 °C (5 min). The gas chromatogram of camelina

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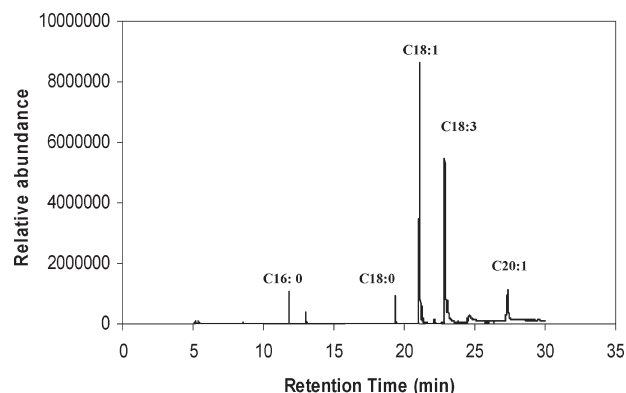


Figure 1. GC chromatogram of camelina biodiesel.

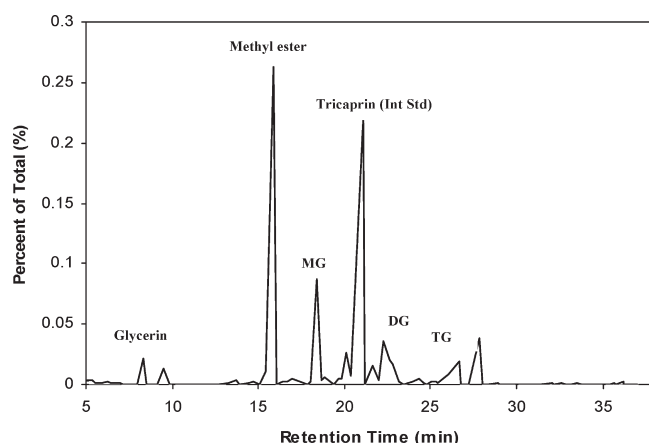


Figure 2. Free and total glycerin GC chromatogram of camelina biodiesel.

Table 1. Textural Characteristics of the Metal Oxide Catalysts

catalyst	BET surface area (m ² /g)	pore volume (cm ³ /g)	pore width (Å)
BaO	0.0760	0.00030	157.984
CaO	5.1262	0.01021	78.973
SrO	0.0637	0.00020	126.419
MgO	10.1941	0.02825	110.877

biodiesel is shown in Figure 1. To determine the free and total glycerin content in the biodiesel, SRI 8610C GC, equipped with a MXT-Biodiesel TG column, was used. The oven temperature program set for SRI GC consists of the following steps: start at 40 °C (3 min) and ramp at 10 °C/min to 380 °C. Figure 2 depicts the free and total glycerin content in the biodiesel, where MG is monoglyceride, DG is diglyceride, and TG is triglyceride. The camelina biodiesel contains a major proportion of esters of mono- and polyunsaturated fatty acids, as shown in Figure 1.

3. Results and Discussion

3.1. Reaction Mechanism. The mechanism of transesterification of triglyceride to biodiesel in the presence of a metal oxide catalyst can be described as follows. In the first step, surface O²⁻ extracts H⁺ from CH₃OH to form CH₃O⁻ (eq 2), which is strongly basic and has catalytic activity in the transesterification reaction.²⁹ In the second step, the carbonyl carbon atom of the triglyceride molecule attracts a methoxide anion from the surface of the MO (M represents Sr, Ba, Ca, and Mg) to form a tetrahedral intermediate (eq 3), where R₁

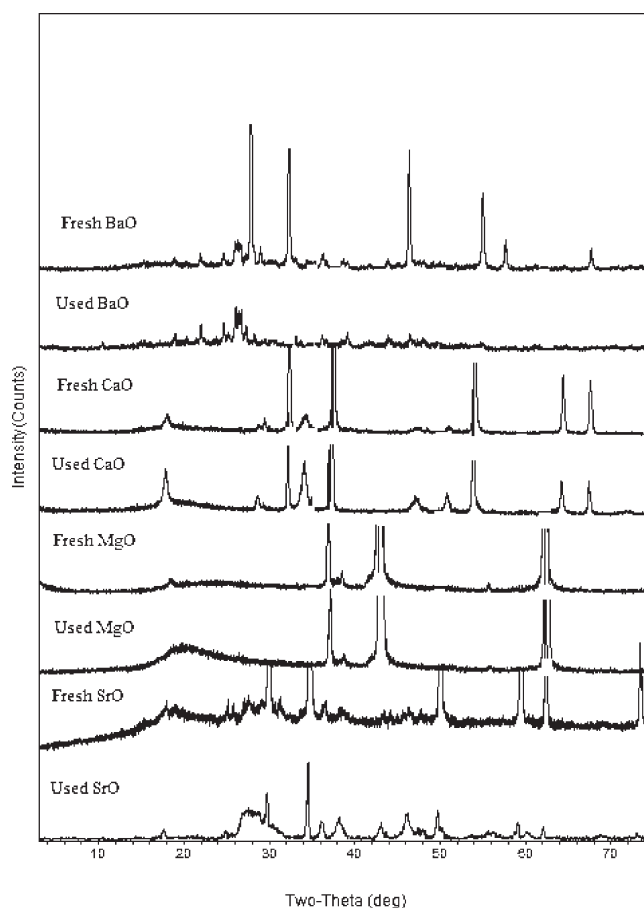
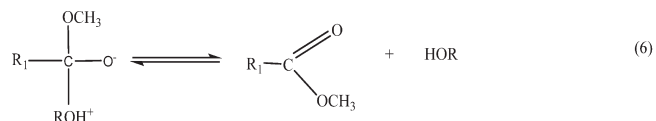
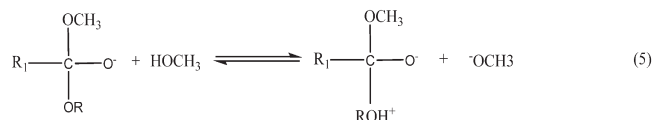
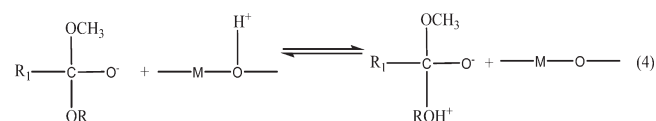
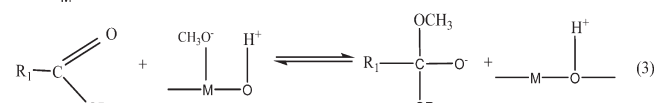
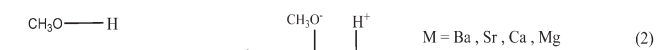


Figure 3. XRD patterns of heterogeneous metal oxide catalysts.

represents the long chain of the alkyl group. In the third step, the tetrahedral intermediate takes H⁺ from the surface of the MO (eq 4). The tetrahedral intermediate can react with methanol to generate methoxide anions (eq 5).¹ In the last step (eq 6), rearrangement of the tetrahedral intermediate results in the formation of biodiesel.²⁵



3.2. Catalyst Characterization. Table 1 shows the textural characteristics of the metal oxide catalyst used for the

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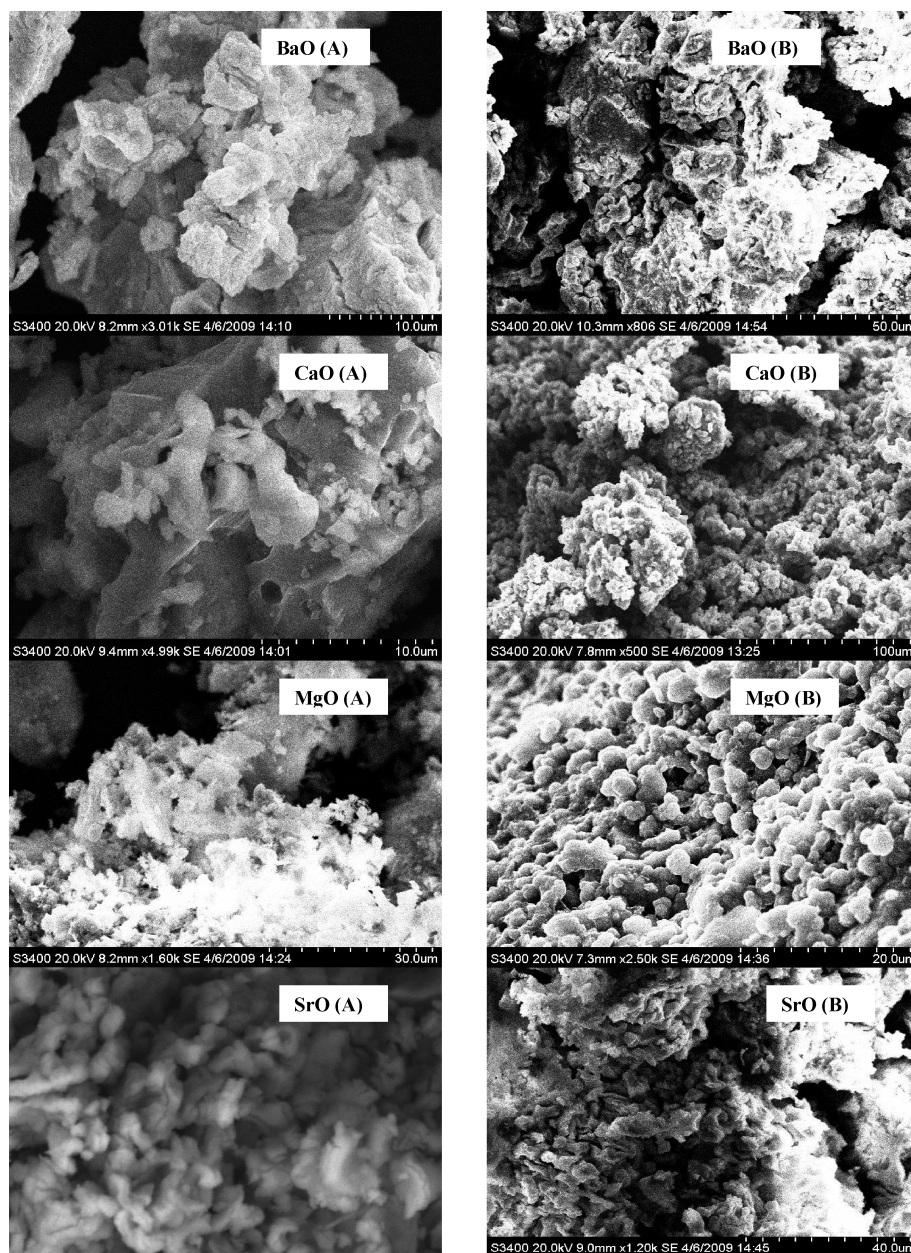


Figure 4. SEM images of metal oxide catalysts: (A) fresh and (B) after the reaction.

transesterification of camellina sativa oil. It was found that MgO and CaO had larger surface areas of 10.1941 and 5.1262 m²/g, respectively, whereas BaO and SrO had the minimum of 0.0760 and 0.0637 m²/g, respectively. However, it was interesting to note that, despite having lower surface areas, BaO and SrO gave the highest biodiesel yield. The order of basic strength and catalyst activity of BaO and SrO catalysts is found higher than CaO and MgO. The catalytic activities increased in the order of MgO < CaO < SrO < BaO. Both the ionic radii and alkalinities of the alkaline earth metals increase in the same order. It suggests that the catalytic activities of alkaline earth metal oxides toward the transesterification are associated with their alkalinities.²³ Besides the specific surface area, acidity/basicity, and acid/base sites, leaching tendencies in biodiesel and selectivity toward the transesterification reaction are also the contributing factors of catalysts in biodiesel formation.^{30,31} These

facts could be the possible reasons of higher activity of SrO and BaO than CaO and MgO, although specific surface areas of BaO and SrO possess a lower value.

The changes in the catalyst structure and integrated intensities of peaks were examined by the XRD. Figure 3 shows the characteristic peaks of the fresh and used metal oxide catalysts.

The peaks of the fresh and used catalysts were compared to know the activity of the catalysts. A slight change in the fresh and used catalyst peaks for CaO and MgO was observed, even after changing in reaction time and reaction temperatures. It suggested that catalyst activity of the fresh catalyst remains the same or differs slightly compared to the used catalyst after the reaction, which means that the catalyst can be reused several times. However, for the fresh SrO and BaO, the catalyst structure was largely different than their respective used catalysts. This illustrated that the order of effectiveness was decreased for the used SrO and BaO catalysts

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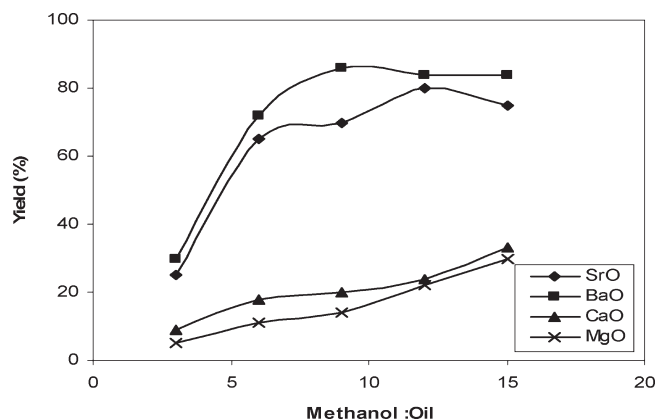


Figure 5. Effect of the methanol/oil molar ratio on the biodiesel yield.

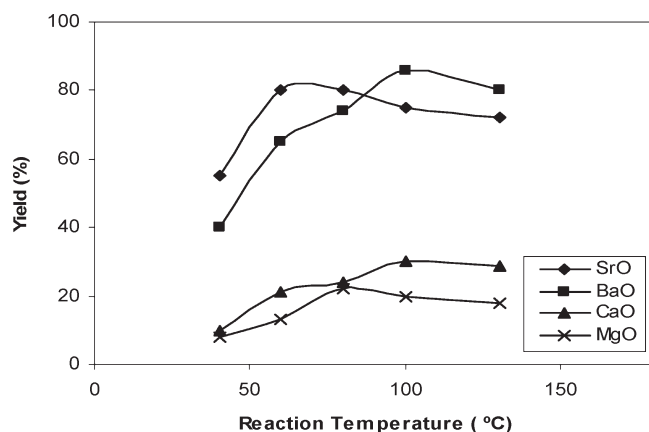


Figure 6. Effect of the reaction temperature on the biodiesel yield.

after the reaction to achieve a maximum yield of biodiesel. The respective used catalysts cannot be used several times to achieve a high yield of biodiesel. The catalytic mechanism of all metal oxides in Group IIA in the periodic table is believed to be the same; however, a slightly different phenomenon was observed in XRD spectra. The changes of XRD spectra of BaO and SrO before and after the reaction were quite different from those of MgO and CaO. These changes in XRD pattern occurred because of the possibility of forming new substances, such as $\text{Ba}(\text{OH})_2$ and $\text{Sr}(\text{OH})_2$ hydroxides, during the reaction because some moisture from the ambient air may have been adsorbed on the catalyst while an appropriate amount is being measured³² or from traces of moisture that remained in the reactor before starting the reaction.

Figure 4 shows the SEM images of fresh and used (after the reaction) metal oxide catalysts. The SEM images taken before and after the reaction by changing reaction parameters showed a similar morphology. Hence, the SEM images do not show a morphological change but rather the regenerable deposition of camelina oil. The surface of the fresh catalysts presents a spongy discrete particle appearance. The deposition of FFAs, crude glycerol, and other impurities on the surface of the catalysts under the reaction conditions was evidenced by SEM observations.

3.3. Reaction Results. *3.3.1. Effect of the Methanol/Oil Molar Ratio on the Biodiesel Yield.* The amount of methanol required for the transesterification was analyzed in terms of

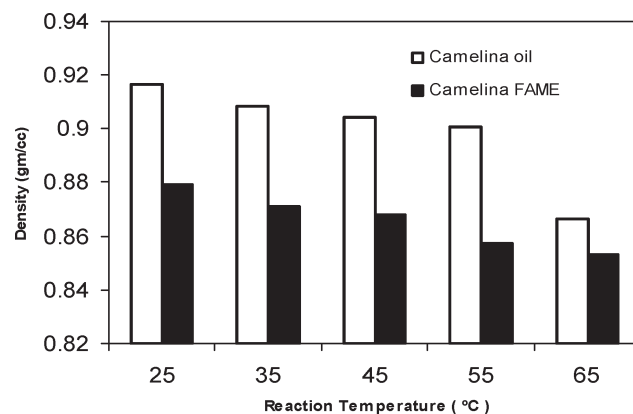


Figure 7. Effect of the temperature on the density of camelina oil and biodiesel.

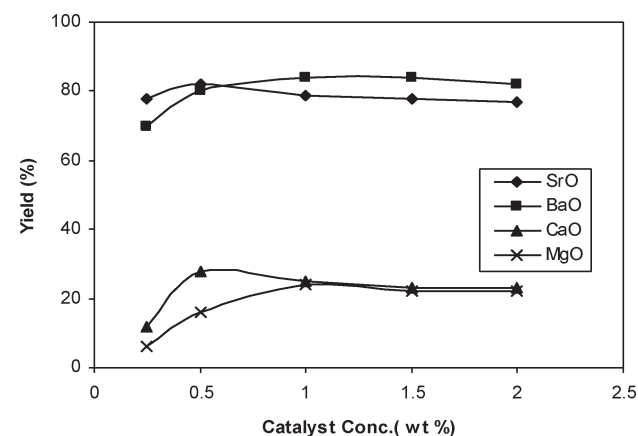


Figure 8. Effect of the catalyst concentration on the biodiesel yield.

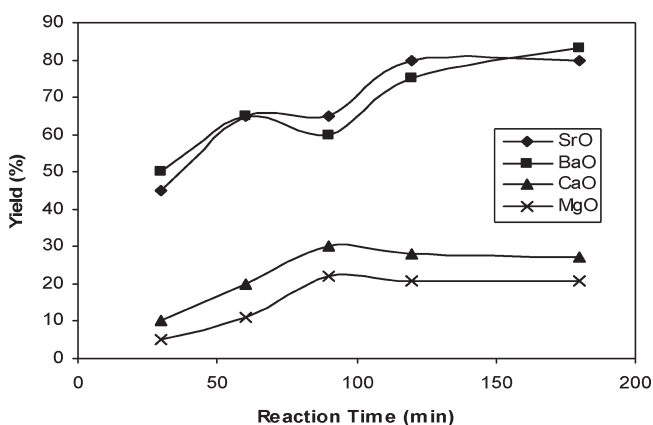


Figure 9. Effect of the reaction time on the biodiesel yield.

the methanol/oil molar ratio. The stoichiometric methanol/oil molar ratio required for a complete transesterification is 3:1. However, in practice, this is not sufficient to complete the transesterification reaction. A higher molar ratio is required to drive the reaction to completion at a faster rate.³³ For this experiment, the methanol/oil molar ratio was changed from 3:1 to 15:1. Figure 5 shows that the reaction rate increased when the molar ratio of methanol/oil was increased. For the BaO catalyst, the maximum yield was

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Table 2. Fuel Properties of Camelina Oil and Camelina Biodiesel

properties	camelina oil	camelina biodiesel	biodiesel standard ASTM D 6751-08	testing methods
specific gravity	0.91 to 0.92	0.87 to 0.88	0.87 to 0.90	ASTM D 287
viscosity (mm ² /s) at 40 °C	14.03 to 15.12	2.9 to 3.15	1.9 to 6.0	ASTM D 445
calorific value (MJ/kg)	44.50 to 46.50	45.05 to 46.15		ASTM D 240
cetane number	35.16 to 36.25	49.26 to 51.17	47 min	ASTM D 613
pour point (°C)	−23 to −20	−11 to −8	−15 to 10	ASTM D 97
flash point (°C)	244 to 260	132 to 140	130 min	ASTM D 93

obtained at a 9:1 molar ratio and then the yield remains the same for the higher molar ratio. For the SrO catalyst, 12:1 is the optimum molar ratio. However, when the amount of the methanol/oil molar ratio was over 12:1, an excess methanol started to interfere in the separation of glycerin because of an increase in the solubility and resulted in the decreasing biodiesel yield.³⁴ The maximum camelina biodiesel yield using CaO and MgO was obtained at an optimum methanol/oil molar ratio of 15:1.

3.3.2. Effect of the Reaction Temperature on the Biodiesel Yield. In the transesterification of heterogeneous catalysts, the reaction proceeds with a three-phase system, oil–methanol–catalyst, in which the reaction rate could slow down because of mass-transfer diffusion resistance.²⁵ However, the reaction rate and biodiesel yield can be increased by increasing the reaction temperature.¹ The reaction temperature was changed within a range of 40–130 °C. For all of the metal oxide catalysts, from Figure 6, the reaction rate was slow at low temperatures. The biodiesel yield increased with an increasing reaction temperature up to a certain level and then decreased. The maximum ester yield for camelina oil using BaO, SrO, CaO, and MgO was obtained at 100, 60, 100, and 80 °C, respectively. At higher temperature, methanol was distilled off and formed a large number of bubbles, which reduce the reaction on the three-phase interface. Furthermore, the influence of the temperature on the densities of camelina oil and camelina biodiesel was studied and shown in Figure 7.

3.3.3. Effect of the Catalyst Concentration on the Biodiesel Yield. High catalytic activity depends upon the catalyst possessing strong basic sites.³⁵ In this study, the catalyst concentration of metal oxides to camelina oil was varied within a range of 0.25–2%. The influence of the catalyst amount on the yield is shown in Figure 8. The maximum yield for camelina oil using BaO, SrO, CaO, and MgO was obtained at 1, 0.5, 0.5, and 1%, respectively. It was observed that the production yield remained the same or slightly decreased with an increased catalyst concentration. At higher concentrations, the intensification of mass transfer became more important than increasing the amount of catalyst.

3.3.4. Effect of the Reaction Time on the Biodiesel Yield. Transesterification experiments for camelina oil were carried out at a constant agitation speed for various periods of times between 30 and 180 min. The maximum yield for camelina oil using BaO, SrO, CaO, and MgO was obtained at 180, 120, 90, and 90 min, respectively. Figure 9 depicts the influence of the reaction time on the yield of biodiesel.

3.4. Fuel Properties of Methyl Esters from Camelina Sativa Oil. The fuel properties of biodiesel from camelina sativa oil

with testing methods are given in Table 2. The viscosity of biodiesel from camelina sativa oil was comparable to regular diesel viscosity, i.e., 2.6 mm²/s. Hence, no hardware modifications are required for handling this fuel (biodiesel) in the existing engine. The cetane number was estimated as 49.26–51.17 and found to be higher than ASTM³⁶ biodiesel standards. A higher cetane number indicates a good ignition quality of fuel. The pour point of camelina biodiesel was found to be between −11 and −8 °C, indicating good compatibility of fuel in the cold season. Fuel consumption and vehicle operation with camelina ester are similar to rapeseed methyl ester.⁹ The free and total glycerin contents in camelina biodiesel were estimated as 0.018 and 0.1195% (% mass). According to ASTM D 6751 biodiesel standards, the free glycerin limit is 0.02% and the total glycerin (free + bound) is 0.24%. The low level of free and total glycerin ensures high conversion of oil to methyl ester.

4. Conclusions

The transesterification of camelina sativa oil using different heterogeneous metal oxide catalysts (i.e., BaO, SrO, CaO, and MgO) was studied for optimum reaction conditions. The metal oxide catalysts used in this study had varying selectivity toward the transesterification reaction depending upon their acid/base-site strength and surface area.

The results of comparative experiments showed that most effective catalyst was BaO and the relative order of effectiveness to transform camelina oil to its ester was BaO > SrO > CaO > MgO. The maximum biodiesel yield for camelina oil using BaO catalyst was obtained at 100 °C, at the reaction time of 3 h, catalyst amount of 1 wt %, and methanol/oil molar ratio of 9:1. Because of its toxicity and noxious properties, BaO has some limitations to use. The SrO catalyst in comparison to BaO could be the better option for further study of the transesterification of camelina oil. The camelina biodiesel has fuel property values relatively closer to that of ASTM biodiesel standards.

The present analysis, optimization, and preliminary evaluation study reveal that the heterogeneous metal oxide catalysts are suitable for the transesterification of camelina oil because of process simplification with minimal environmental problems. However, additional research on new basic solid catalysts, catalyst stability and regeneration, kinetic study, and analysis using a biodiesel-fueled engine is recommended.

Acknowledgment. This project was partially supported by the New Mexico State University Office of Vice President for Research and State of New Mexico through a New Mexico Technology Research Collaborative Grant.

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