



Short Communication

Biodiesel production using alkali earth metal oxides catalysts synthesized by sol-gel method

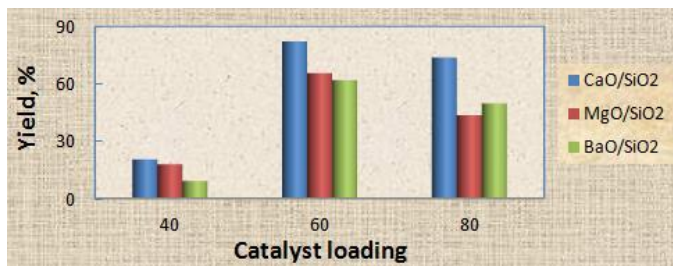
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HIGHLIGHTS

- Catalyst loading was studied for different catalysts ranging.
- Different alkali earth metal oxides doped SiO₂ as catalyst for the biodiesel production.
- Synthesis of catalysts using the sol-gel method.

GRAPHICAL ABSTRACT



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ABSTRACT

Biodiesel fuel is considered as an alternative to diesel fuel. This fuel is produced through transesterification reactions of vegetable oils or animal fat by alcohols in the presence of different catalysts. Recent studies on this process have shown that, basic heterogeneous catalysts have a higher performance than other catalysts. In this study different alkali earth metal oxides (CaO, MgO and BaO) doped SiO₂ were used as catalyst for the biodiesel production process. These catalysts were synthesis by using the sol-gel method. A transesterification reaction was studied after 8h by mixing corn oil, methanol (methanol to oil molar ratio of 16:1), and 6 wt. % catalyst (based on oil) at 60°C and 600rpm. Catalyst loading was studied for different catalysts ranging in amounts from 40, 60 to 80%. The purity and yield of the produced biodiesel for 60% CaO/SiO₂ was higher than other catalysts and at 97.3% and 82.1%, respectively.

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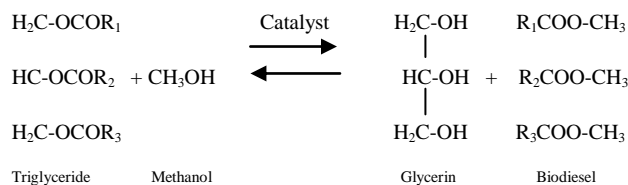
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1. Introduction

Nowadays, fuels are an inevitable part of industrial machinery development and growth of any country. This economic development has led to a huge demand for energy the major part of which is derived from fossil sources such as petroleum, coal and natural gas. However, the limited reserve of fossil fuels has prompted many researchers to look for alternative fuels which can be produced from renewable feedstock. Biodiesel (a mixture of fatty acid methyl esters (FAMES)) as a cleaner renewable fuel is considered as the better option because of its environmental friendly characteristics while giving almost the same functional properties as fossil fuels (Semwal et al., 2011). Various methods have been implemented for the production of biodiesel from plant oils (such as: soybeans, peanuts, rapeseed, palm, corn, sunflower, sorghum, canola, cottonseed and etc.), recycled cooking greases or oils, used cooking oils and restaurant frying oils, or animal fats (such as: beef, tallow, poultry fats, fish oils, pork lard and etc.). Because plants produce oils from sunlight and air, and can do so year after year on cropland, these oils are considered renewable (Van Kasteren and Nisworo, 2007).

The other advantages of biodiesel are that it is nontoxic, biodegradable, suitable for sensitive environments, and can reduce global warming gas emissions (Bhatti et al., 2008; Viola et al., 2012). Today, most biodiesel is produced through the transesterification of triglycerides using alcohol and a catalyst (homogeneous or heterogeneous bases or acids), as in Eq. (1).



Generally, the transesterification reaction is carried out at 60–80°C (Di Serio et al., 2007). However, the major hurdle in the commercialization of biodiesel is chiefly due to the non-availability of crude material and the cost of processing (Kondamudi et al., 2011). Production costs are still rather high; as compared to petroleum diesel (Di Serio et al., 2007). The use of homogeneous catalysts requires purification steps and extensive conditioning for the biodiesel and glycerol to separate the catalysts (Jacobson et al., 2008). In contrast to homogeneous catalysts, heterogeneous catalysts in the transesterification process of biodiesel production have recently attracted more attention (Chen et al., 2012). This is because they can be easily separated from the reaction medium due to their immiscibility with either of the reaction products (Di Serio et al., 2007; Lima et al., 2012). Biodiesel production costs can be reduced by using heterogeneous catalysts (Di Serio et al., 2007; Jegannathan et al., 2008; Agarwal and Bajaj, 2009). This heterogeneous process will supply higher quality biodiesel and glycerol, which are more easily separable, obviate expensive refining processes, and can potentially overcome the drawbacks in the transesterification process of biodiesel production (Chen et al., 2012). In general basic heterogeneous catalysts increase the yields of the transesterification process and speed up the reaction rate compared to solid acid catalysts and selectively respond with glycerides. The presence of free fatty acid does not influence the solid base of the catalyzed transesterification process (Lotero et al., 2006). Furthermore, basic heterogeneous catalysts need feedstock with low free fatty acids in order to prevent deactivation of the catalyst, since they are very sensitive to the presence of water and free fatty acids. Also, acidic heterogeneous catalysts can be applied to feedstock with high water and free fatty acid content. Moreover, solid acid catalysts require higher temperatures and higher catalyst loadings to achieve reasonable biodiesel yields (Schuchardt et al., 1998).

The type of precursor of active materials also has a significant effect on the catalyst activity of supported catalysts. The effect of the catalyst precursor by comparing the activity of $\text{Al}_2\text{O}_3/\text{K}$ synthesized by two different potassium precursors was reviewed by Zabeti et al. (2009). For reactions with the same conditions although the basicity of $\text{Al}_2\text{O}_3/\text{KI}$ was less than the basicity of $\text{Al}_2\text{O}_3/\text{KNO}_3$, more conversion was obtained using $\text{Al}_2\text{O}_3/\text{KI}$ which is an

indication of the effect of the precursor type on the catalyst activity (Zabeti et al., 2009).

Generally the most significant advantages are in using solid catalysts this is because non-polluting by-products are formed, and the environmental problems caused by their alkaline or acidic characteristics can minimize corrosion and they do not require further purification procedures (Lima et al., 2012).

Many alkali earth and metal oxides have been studied for the transesterification of different oils. Kawashima et al. (2008) investigated different types of metal oxides containing Ba, Ca, Mg, or La for the transesterification reaction of turnip oil at 60°C with a 6:1 molar ratio of methanol to turnip oil for 10h. Best results were obtained using CaMnO_3 , $\text{Ca}_2\text{Fe}_2\text{O}_5$, CaZrO_3 , and CaCeO_3 , with the catalytic basicities ranging from 7.2 to 9.3 and showing 92%, 92%, 88%, and 89% yields of biodiesel, respectively (Kawashima et al., 2008).

In this study, the catalytic reactivity of alkaline earth metal oxides including, CaO/SiO_2 , BaO/SiO_2 and MgO/SiO_2 with the loadings of 40, 60, and 80 wt. % prepared using sol-gel method, were evaluated by transesterifying corn oil and methanol. The most active metal oxides were chosen to prepare a SiO_2 catalyst for developing a high-performance solid base catalyst, which could convert corn oil to biodiesel with a purity of over 98%. The transesterification process of corn oil at 60°C with a 16:1 molar ratio of methanol to corn oil 6 wt. % catalyst concentrations (based on oil) was carried out at 600rpm and at reflux temperature for 8h in a batch reactor. The reaction conditions were optimized in the final phase of the study (Hojabri, 2012).

2. Materials and methods

2.1. Materials

In the synthesis of catalysts, magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99-102%, Merck) was used as a precursor for magnesium oxide, calcium nitrate tetra hydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 99-102%, Merck) was used as precursor for calcium oxide and barium nitrate ($\text{Ba}(\text{NO}_3)_2$, 99%, Merck) was used as a precursor for barium oxide. Tetraethyl orthosilicate (TEOS) (>99%, Merck) were used as precursors for silica support oxides. Deionized water (DIW) was used as the solvent and hydrochloric acid (37%, Merck) and ammonia solutions (25 %, Merck) were used as peptizer in the sol-gel method. Also methanol (99.8%) was purchased from pars chemical Co. and corn oil purchased from a local supermarket. Corn oil had 195.7 mg KOH/g oil saponification index and 0.12 wt. % free fatty acid. The average molecular weight of corn oil was 860 g/mol, calculated from the saponification value. Other properties of corn oil can be seen in Table 1.

2.2. Preparation of catalysts doped SiO_2

CaO/SiO_2 , MgO/SiO_2 and BaO/SiO_2 catalysts were prepared using the sol-gel method. The CaO/SiO_2 preparation processes were as follows: calcium nitrate tetra hydrate and TEOS and HCl 1M were dissolved in DIW in a glass beaker under vigorous stirring at 400rpm for 2h at 65°C. The addition of an ammonia solution to the mixture led to the formation of a solid precursor suspended in the solution. The gel was kept in the beaker after the solvents were evaporated completely at 75°C for 5h. The particle was denoted as CaO/SiO_2 after drying the precursor at 110 °C for 20h and then calcination at 650°C for 3h. This calcination procedure was optimized in the Hojabri (2012) study. The same procedure was applied to synthesize MgO/SiO_2 and BaO/SiO_2 catalysts, but magnesium nitrate hexahydrate and barium nitrate were used as the precursors for MgO and BaO, respectively. The process of catalysts synthesis was acquired from Umdu et al. (2009) study.

2.3. Catalysts characterization

The synthesized catalyst CaO/SiO_2 , MgO/SiO_2 and BaO/SiO_2 were characterized by an X-ray diffraction (XRD) analysis. The analysis of the XRD was carried out by radiation of Cu K α . Intensity versus 2-theta were plotted at 10-110° by step of 0.03°.

2.4. Transesterification process

The catalyzed transesterifications were carried out at 60°C and 600rpm for 8h. For all reactions, the reaction mixture consisted of corn oil, methanol and solid catalyst 6 wt. %, with respect to oil. The molar ratio of corn oil to methanol was maintained at 1:16. Experiments were carried out in a 250mL two necked flask by using a thermometer and condenser. After each reaction, the catalyst was separated by using a centrifuge. The produced glycerol and biodiesel were then separated from each other by using a separation funnel. To improve the purity of the produced biodiesel, the mixture was washed with water at 90°C several times and finally, to remove the residual water it was placed in an 110°C oven for 2h.

2.5. Purity and yield of produced biodiesel

A characterization of FAME in biodiesel samples was carried out by using an HP 6890 gas chromatograph with a flame ionization detector (FID). The capillary column was a BPX-70 with a length of 120m, film thickness of 0.25µm and internal diameter of 0.25mm. Nitrogen was used as the carrier gas and also auxiliary gas for the FID. 1µL of the sample was injected by a 6890 Agilent Series Injector. The inlet temperature of the sample into injector was 50°C which was heated to 230°C. Methyl laurate (C12:0) was added into biodiesel as a reference and the samples were analyzed by Gas Chromatography (GC), that was mentioned above. Weight percent of FAME or purity of biodiesel was defined as Eq. (2):

$$\text{Purity (\%)} = \frac{\text{area of all FAME}}{\text{area of reference}} \times \frac{\text{weight of reference}}{\text{weight of biodiesel sample}} \times 100$$

The biodiesel yield was calculated by using Eq. (3):

$$\text{Yield (\%)} = \frac{\text{area of all FAME}}{\text{area of reference}} \times \frac{\text{weight of reference}}{\text{weight of biodiesel sample}} \times \frac{\text{weight of biodiesel produced}}{\text{weight of oil used}} \times 100$$

3. Results and discussions

Figure 1 provides an overview of the XRD pattern of 60% CaO/SiO₂, 60% MgO/SiO₂ and 60% BaO/SiO₂ catalysts, which were calcined at 650°C for 3h. According to Figure 1-a, the main diffraction peaks belonged to SiO₂ and CaO. SiO₂ presented its main diffraction peaks at 2θ=23.365, 29.808, 41.784 and 43.294 while CaO displayed its main diffraction peaks at 2θ=23.988, 29.777, 32.665, 37.642 and 67.798. Figure 1-b shows the main diffraction peaks for MgO and SiO₂. For SiO₂ these peaks were seen at 2θ=35.254, 36.532, 42.884, 52.178, 53.137, 62.272 and 78.299 while for MgO the main diffraction peaks became present at 2θ=37.242, 43.168, 62.615, 75.125 and 79.158. Figure 1-c also illustrates the diffraction peaks for BaO and SiO₂. The SiO₂ displayed the main diffraction peaks at 2θ=28.607, 29.869, 52.178 and 56.519 and the main diffraction peaks for BaO were presented at 2θ=26.349, 27.031, 43.137, 54.216 and 76.898. As it can clearly be seen in these figures (Figures 1-a to 1-c), a calcination temperature of 650°C produced CaO, MgO and BaO crystalline. Also the peaks relating to CaO and MgO were sharp, but BaO had small peaks. These peaks illustrate that the performance of CaO and MgO catalysts was more than the BaO catalyst. In other words the XRD pattern for MgO/SiO₂ shows many peaks in relation to SiO₂, which indicates an unsuitable dispersion of MgO on SiO₂ support.

3.2. Properties of biodiesel

The various biodiesel properties produced by 60 % CaO/SiO₂, 60 % MgO/SiO₂ and 60 % BaO/SiO₂ have been studied and provided in Table 1. Also a comparison of the properties for the derived biodiesels with ASTM D6751 is given in this table. It can be seen from the data that the biodiesels properties (density at 15 °C, kinematic viscosity at 40 °C, pour point and cloud point) are comparable with standard values with ASTM D6751. Table 1 also provides information regarding the methyl ester content (biodiesel purity) of the produced biodiesel by using a 60 % CaO/SiO₂, 60 % MgO/SiO₂ and 60 % BaO/SiO₂ catalysts.

3.3. Catalyst loading effect

The effect of catalyst loading on the purity and yield of the produced biodiesel was investigated by using a methanol to oil molar ratio of 16:1 at 60°C for 8h. This parameter (catalyst loading) varied at a range of 40% to 80%. As shown in Figures 2 and 3, the maximum values of purity obtained from using CaO/SiO₂, MgO/SiO₂ and BaO/SiO₂ catalysts were related to catalyst loading of 60%. At catalyst loading of 60%, the purity of the produced biodiesel using CaO/SiO₂, MgO/SiO₂ and BaO/SiO₂ catalysts were equal to 97.3%, 81.4% and 79.7%, respectively. Also the yields for the produced biodiesel at catalyst loading 60% for CaO/SiO₂, MgO/SiO₂ and BaO/SiO₂ catalysts were equal to 82.1%, 65.5% and 61.9%, respectively. So, the maximum purity and yield of the produced biodiesel was obtained by utilizing 60% CaO/SiO₂ catalyst and equaled to 97.3% and 82.1%, respectively. Therefore, the performance of the catalyst was found to be as follows: CaO/SiO₂>MgO/SiO₂>BaO/SiO₂.

Table 1

Properties of the produced biodiesels in comparison to biodiesels derived through an ASTM D6751 standard.

Property	Corn oil	Biodiesel			ASTM D6751
		60 % CaO/SiO ₂	60 % MgO/SiO ₂	60 % BaO/SiO ₂	
Density at 15 °C, g/cm ³	0.921	0.887	0.873	0.885	0.86 to 0.90
Viscosity at 40 °C, mm ² /s	21.13	4.40	4.52	4.37	4 to 6
Pour Point, °C	14	5	6	6	-15 to 10
Cloud Point, °C	18	8	8	8	-3 to 12
Methyl ester content %	-	97.3	81.4	79.7	-

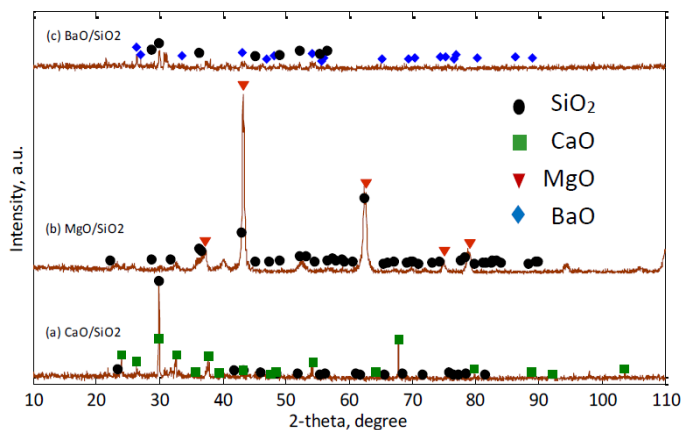


Fig. 1. XRD pattern of 60% CaO/SiO₂, 60% MgO/SiO₂ and 60% BaO/SiO₂ catalysts calcined at 650°C.

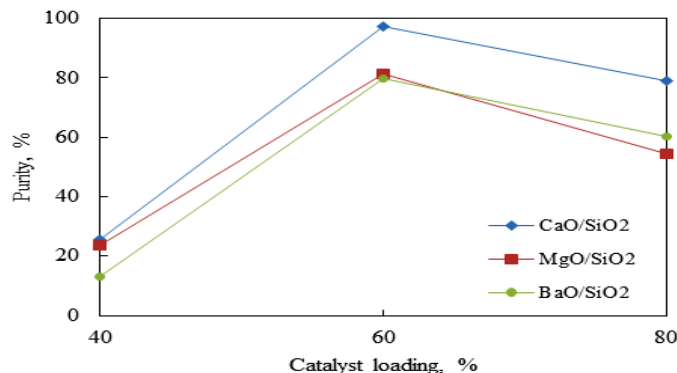


Fig. 2. Purity of produced biodiesel versus catalyst loading, for CaO/SiO₂, MgO/SiO₂ and BaO/SiO₂ catalysts.

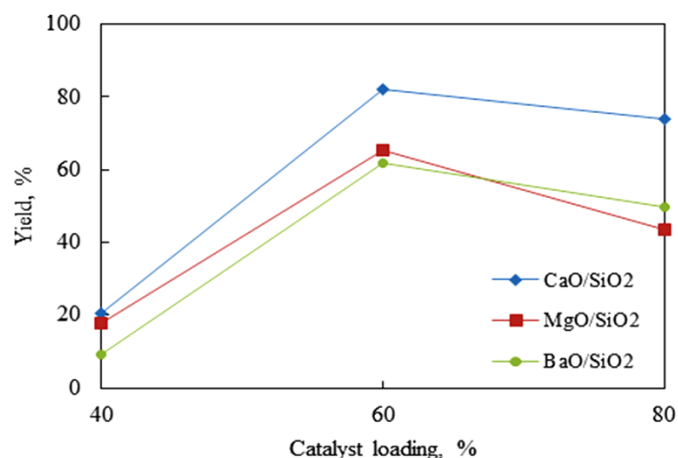


Fig. 3. Yield of produced biodiesel versus catalyst loading, for CaO/SiO₂, MgO/SiO₂ and BaO/SiO₂ catalysts.

4. Conclusions

In this study CaO/SiO₂, MgO/SiO₂ and BaO/SiO₂ catalysts were used for biodiesel production from corn oil. Sol-gel method was used for the synthesizing of catalysts. The catalysts were synthesized at different catalyst loadings (40%, 60% and 80%). The calcination temperature of catalysts was equal to 650°C. The transesterification reaction was carried out from a mixture of corn oil, methanol (methanol to oil molar ratio of 16:1) and 6 wt. % of catalyst in respect to corn oil, at 60°C and for a time period of 8h. Although the basic strength increased in the following order MgO<CaO<BaO, however the study found that alkali metal oxides supported by SiO₂ and catalyst precursors had an impact on catalyst activity. The XRD pattern for these catalysts was shown in this amount of catalyst loading, CaO and MgO had sharper peaks than BaO. Moreover the XRD pattern for the MgO/SiO₂ catalyst showed many peaks for the SiO₂, which was due to the unsuitable dispersion of catalyst on the precursor. Results showed that, maximum values of purity and yield could be obtained at catalyst loading of 60% for CaO/SiO₂, MgO/SiO₂ and BaO/SiO₂. Also the purity and yield of the produced biodiesel by using a CaO/SiO₂ catalyst was higher than other catalysts and equaled to 97.3 % and 82.1 %, respectively.

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