*Regular Article*

# Synthesis of KOH@CaO Catalyst by Sol-gel Method for Highly Efficient Biodiesel Production from Olive Oil

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In this research, biodiesel was produced from olive oil in the presence of KOH-impregnated CaO catalyst (CaO@KOH). To this end, CaO catalyst was produced using the sol-gel method. The percent composition of fatty acids (FAs) in olive oil was measured using gas chromatography (GC) analysis. Also, SEM and BET analyses were performed to evaluate the surface properties of the catalyst. The results indicated that the biodiesel conversion yield of 99 ± 0.2% was obtained under the optimal conditions; *i.e.,* an oil/methanol ratio of 1:15, a catalyst dosage of 1.5 wt.%, a reaction temperature of 65 °C, and a reaction time of 4 h, which was the highest biodiesel yield ever achieved from olive oil. The reusability of the catalyst was further investigated through 8 successive cycles of biodiesel generation, and the results indicated that the reduction of biodiesel conversion yield was less than 2% after 4 cycles of reusing the catalyst, confirming the high potential of the aforementioned catalyst. Also, the production cost of the KOH/CaO catalyst was calculated to be 108.45 USD/Kg, which had a reasonable cost. Moreover, the physical properties of the produced biodiesel were within the standard range.

**Keywords:** Biodiesel, Olive oil, Calcium oxide catalyst, Potassium hydroxide, Transesterification process

## INTTRODUCTION

Today's world is encountering an energy crisis where the limited resources of fossil fuels are likely to fail to satisfy the ever-increasing demand for energy. The reduction in the reserves of fossil fuels, the ever-increasing consumption of the fossil fuels, and the increased prices of oil and its derivatives, in one hand, and concerns about the increased amount of environmental pollution upon combustion of the fossil fuels, on the other hand, have led the humans toward searching for alternative sources of energy at affordable prices [1-2]. The biodiesel offers a number of advantages over fossil fuels, including non-toxicity, biodegradability, negligible contents of sulfur and aromatic compounds, comparative energy content to that of oil, and biocompatibility [3]. The biodiesel can be directly

used in the internal combustion engines as its characteristics closely mimic those of the engine diesel, while the use of the biodiesel minimizes the emission of carbon monoxide (CO), suspended fine particles, and unburnt hydrocarbons (HCs). In addition, the biodiesel is known to provide a higher cetane number together with higher combustion efficiency than the conventional diesel. With a higher flash point than the conventional diesel, the biodiesel is less volatile yet safer to transport and use. The biodiesel contains oxygen at 10-12 wt.%, which improves the combustion process inside the engine [4-5].

The biodiesel is a compound of long-chain mono-alkyl esters with the fatty acids (FAs) produced upon the reaction of an alcohol with some renewable lipid. For the most part, the renewable lipid is extracted from the animal fats including the chicken fat or lamb fat as well as herbal oils such as olive oil, jatropha oil, soybean oil, cottonseed oil, and/or cooking oil [6]. A major portion of such oils is

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comprised of triglycerides, leading to the production of not only some esters, but also another valuable product: glycerin. All over the world, the biodiesel is yet to be recognized as a public fuel resource, mainly because of its higher cost compared to the fossil fuels. Among others, the unavailability of affordable supplies of the biodiesel is the most significant barrier limiting the commercialization of the biodiesel [2].

The biodiesel generation has been practiced through a number of various methods, including the dilution, pyrolysis, microemulsion, and transesterification. The transesterification process has become the best method for high-quality biodiesel generation [7]. The transesterification is a chemical process where triglyceride reacts with alcohol in the presence of catalyst. Various alcohol species have been used for the transesterification process, including ethanol, methanol, propanol, and butanol. Many studies have shown that the methanol is a preferred alcohol for the transesterification process thanks to its lower cost, physical and chemical advantages, and easy separation from the glycerol [8]. The transesterification process has been studied using various catalysts, including alkali, acidic, and enzymatic catalysts. However, the alkali catalysts have been mostly the catalysts of choice for the transesterification reaction as the process becomes too slow when an acidic catalyst is used. The transesterification is known to be influenced by particular parameters, including the methanol-to-oil ratio, the reaction temperature, the reaction time, and the catalyst type and dosage [9-10].

Some disadvantages of biodiesel generation using homogenous basic catalysts include the intensive energy consumption and the high costs of catalyst separation and purification. Also, acidic catalysts require high temperatures and long reaction times to achieve high biodiesel yield [6]. Accordingly, heterogeneous solid catalysts have been used to reduce the cost of purification process; these include metal oxides, zeolites, hydrotalcites and γ-alumina. The use of such catalysts has been promoted due to the ease of separating them from the reaction mixture and their reusability. In many cases, these catalysts are either alkali or alkali oxides supported on a large-specific surface area support. Similar to the homogeneous catalysts, the solid basic catalysts are more active than the solid acidic

catalysts. The calcium oxide (CaO) has been acknowledged as a highly active catalyst for the transesterification process. The synthesis of biodiesel using a heterogenous, rather than a homogenous, solid catalyst can potentially lower the process cost, because such catalysts are reusable and provided for performing the reaction in a fixed bed through a continuous process [11]. There are various types of catalysts for biodiesel generation including MgO [1,5], $CaO/CuFe_2O_4$ [6], CaO/MgO [10], CaO [11], KOH, NaOH [12] and lipase [13].

The present research was aimed at producing the biodiesel from olive oil using a potassium hydroxide (KOH)-impregnated CaO catalyst. We further evaluated the effects of different parameters on the biodiesel conversion efficiency, including the reaction temperature, the reaction time, the catalyst type and dosage, and the methanol/oil ratio, to find the optimum set of conditions. Subsequently, the produced biodiesel was blended with the petro-diesel at different ratios and the physical properties of the resultant blends such as pour point, flash point, cloud point, viscosity, density and cetane number were assessed and compared with international standards. According to the authors' knowledge, there is no study in the literature using the KOH@CaO catalyst for biodiesel production and this catalyst is synthesized and used for the first time in the transesterification process of olive oil.

## MATERIALS AND METHODS

### Chemicals

To synthesize the CaO catalyst, the calcium nitrate tetrahydrate $(Ca(NO_3).4H_2O$, with a purity of 99.9%), ethylene glycol $(HOCH_2CH_2OH$, with a purity of 99.9%), sodium hydroxide (with a purity of 97%), and potassium hydroxide (with a purity of 97%) were procured from Merck Company (Germany). Also, methanol was purchased from Mojallali Company (Iran, purity = 99.5%).

### Required Material

In this work, the biodiesel generation was performed from the pure olive oil procured from the local market. The composition of the FAs in the olive oil was determined *via* gas chromatography (GC) analysis, as reported in Table 1.

**Table 1.** Composition of the FAs of the Olive Oil, as per GC Analysis

| Compound name | Molecular formula | Molar mass | Amount (%) |
|---|---|---|---|
| Myristic acid | $C_{14}$:0 | 228.3 | 0.1 |
| Palmitic acid | $C_{16}$:0 | 256.42 | 13 |
| Palmitoleic acid | $C_{16}$:1 | 254.41 | 1.3 |
| Margaric acid | $C_{17}$:0 | 270.45 | 0.07 |
| Stearic acid | $C_{18}$:0 | 284.48 | 0.24 |
| Oleic acid | $C_{18}$:1 | 282.47 | 74.54 |
| Linoleic acid | $C_{18}$:2 | 280.45 | 8.09 |
| Linolenic acid | $C_{18}$:3 | 278.44 | 0.2 |
| Arachidic acid | $C_{20}$:0 | 312.53 | 0.55 |
| Eicosenoic acid | $C_{20}$:1 | 310.51 | 1.15 |
| Docosanoic acid | $C_{22}$:0 | 340.58 | 0.67 |
| Nervonic acid | $C_{24}$:1 | 366.62 | 0.01 |

## Synthesis of CaO Nanoparticles Using the Sol-gel Method

In this study, firstly, 11.81 g of the calcium nitrate tetrahydrate was mixed into 25 ml of the ethylene glycol and the mixture was stirred using a magnetic stirrer for 1 h. Subsequently, 2 g of sodium hydroxide was dissolved in 25 ml of distilled water in a burette and it was then added to the former solution under stirring in a dropwise fashion. After 15 min of stirring, when the initial mixture took some gel-like form, it was left in stationary for 5 h to reach a white gel. The white gel was then washed with distilled water. To this end, 1 l of distilled water was heated to 70 °C and then mixed with the sample. The mixture was left in stationary to have its sodium hydroxide well mixed with the water and then precipitated in the form of a powder. After about 1 h, when the gel was turned into the powder and precipitated, the water was removed in such a way to avoid discharging the powder, with the residual water discharged by a syringe to the point where the powder was almost completely dehydrated. In order to remove the water completely to achieve dry powder, the hydrated powder was dried in an oven at 110 °C for 12 h. Finally, calcination was performed by placing the sample in an electric furnace at 800 °C for 4 h. The prepared catalyst was characterized by scanning electron microscopy (SEM, on a TECSCAN Mira) and BET analyses. Moreover, the morphological structure and particle size distribution of the CaO catalyst were evaluated using SEM analysis. BET analysis was further conducted to measure the specific surface area of the samples.

Performing several experiments for producing the biodiesel from the olive oil in the presence of the CaO catalyst, the biodiesel conversion yields were compared to those with catalyst impregnation. Based on the outcomes of the experimental tests, it was figured out that the impregnated CaO catalyst was more efficient than the original CaO catalyst. Accordingly, the rest of analyses in this research were performed on the biodiesel generation from olive oil in presence of the impregnated CaO catalyst.

## Impregnation of the CaO Particles with KOH

First, a 1 M KOH solution was prepared. To this end, 11.56 g of KOH was dissolved in 1 l of distilled water. Next, the CaO particles were mixed with 200 ml of solution per gram of the CaO. The mixture was stirred using a magnetic stirrer for 2 h. Subsequently, the result was left in stationary to have its powdery content precipitated. The precipitated powder was then completely dehydrated in an oven at 300 °C for 2 h. Finally, the dried powder was used as catalyst in the biodiesel generation process.

## Economical Assessment of the Catalyst Production

In this section, the cost of the catalyst produced is calculated. The details of prices are given in Table 2. The cost of electricity in Iran is 175 IRR for 1 KW/H, which is equal to 0.004164 USD. Also, a heater-stirrer consumes 800 watts energy per 1 h. So, its cost will be 0.00333 $. In this study, the magnetic stirrer was used for 1 h and 15 min. Moreover, the oven power supply has 800 watts and 220 volts, which was used for 12 h. Furthermore, the power supply is about 4.5 kW in most of the furnace in the range 1200-1400 °C and the furnace worked for 4 h, which its cost is calculated as 4h × 4.5 KW × 0.004164 USD = 0.074952 $. In conclusion, the sum of the total prices will be as follows:

Total cost = 1.36027 $ + 0.3125 $ + 0.0033312 $ + 0.008328 $ + 12*0.0033312 + 0.074952 $ + 0.39859 $ + 2*0.0033312 $ + 2*0.0033312 $ + 0.5 $ = 2.71127 $

This cost has been achieved for about 25 g of catalyst. Therefore, the production cost for 1 kg of the KOH/CaO catalyst is about 108.45 $.

## Biodiesel Production Process

To produce biodiesel from the olive oil, the transesterification process was practiced in the presence of the CaO catalyst. To prevent the methanol evaporation and loss, a reflux system including a condenser was used. . The condenser could also be devised to take a better control over the temperature. Once the reflux system was initialized, 50 g of the olive oil was spilled into a three-neck flask and heated to 65 °C. Then, methanol was added to the oil at a methanol-to-oil ratio of 1:15. In order to facilitate the transesterification reaction, some catalyst was added to the mix at 1.5 wt.%. A magnetic stirrer was used to stir the mixture. In this work, the stirring rate was constant at 500 rpm for all stages. The mixture temperature was measured by a thermometer every 5 min. It is worth mentioning that, the methanol and catalyst should be thoroughly mixed before being added to the olive oil at 65 °C. Upon expiry of the reaction time (4 h), the produced biodiesel and glycerol were transmitted to a decanter funnel where the separation process took 24 h to accomplish. After 24 h, the solution in the funnel was decomposed into three phases, the biodiesel, glycerol, and catalyst phases. Upon separating the produced biodiesel, it was filtered through Whatman filter paper to remove the associated glycerol or catalyst, if any. Knowing that the catalyst used in this work was impregnated with KOH and acknowledging the soaping effect of the KOH, the produced biodiesel was washed several times with normal water until the discharged water was colorless with no trace of soap in the water. Finally, the produced biodiesel was prepared for further analysis and actual use. Each test was performed in triplicates and the biodiesel conversion yield was obtained *via* Eq. (1):

$$Biodiesel\ conversion\ (\%) = \frac{Weight\ of\ produced\ biodiesel}{Weight\ of\ oil} \times 100$$

(1)

The transesterification process of triglycerides includes three sequential and reversible reactions where triglyceride reacts with methanol to produce monoglycerides, diglycerides, and eventually glycerol and biodiesel (FAME) according to Eq. (2) [14].
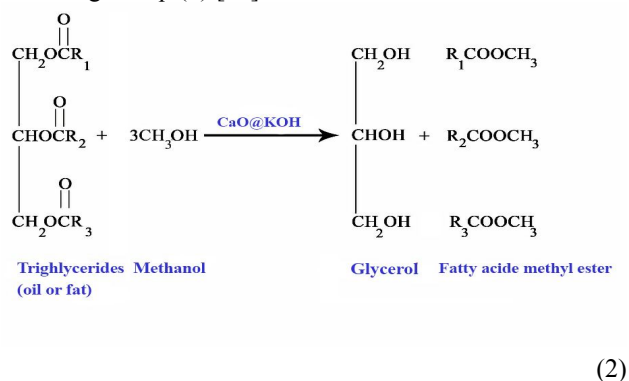


(2)

**Table 2.** The Cost of Chemical Used in this Study for the Production of KOH/CaO Catalyst

| Chemicals | Price | The amount used |
|---|---|---|
| KOH | 34.48 $/kg | 0.39859 $ for 11.56 g |
| Calcium nitrate tetrahydrate | 115.18 $/kg | 1.36027 $ for 11.81 g |
| Eethylene glycol | 12.5 $/kg | 0.3125 $ for 25 ml |
| Sodium hydroxide | 0.5 $/kg | 0.001 $ for 2 g |
| Distilled water | 0.1 $/l | 0.5 $ for 5 l |

In the next step, physical properties of the produced biodiesel were obtained, including the density, viscosity, flash point, cloud point, and pour point. The density and viscosity measurements were performed using an SVM 3000 apparatus. The flash point was measured by the so-called Pensky-Martens closed-cup flash-point test, while the cloud and pour points were examined according to ASTM D97. Subsequently, the characteristics of the produced biodiesel were compared with the reference values provided in the respective international standard codes, including ASTM D6751 and EN14214.

## RESULTS AND DISCUSSION

### Characterization of the Catalyst

In order to evaluate the size of the synthesized CaO particles, SEM analysis was performed. Figure 1 shows the SEM images of the CaO catalyst in two scales of 200 nm and 1 micron. As shown, the particles of the CaO catalyst are spherical. The SEM analysis further demonstrates that the catalyst has particles of different sizes. Also, there are many pores and holes on the surface of the catalyst, which are very efficient in the transesterification process. Moreover, Fig. 2 shows SEM images of the KOH-impregnated CaO catalyst. This figure indicates that the catalyst has a large number of small pores, making it preferable for the transesterification process and biodiesel generation. Moreover, a majority of the catalyst particles are herein observed to be nano sized.

BET analysis was performed to measure the specific surface area of the catalyst. The results showed that the CaO catalyst possessed a specific surface area, pore volume, and pore size of 73.12 $m^2$ $g^{-1}$, 0.0105 $cm^3$ $g^{-1}$, and 3.25 nm, respectively. After the impregnation in KOH, the surface properties changed to 113.7 $m^2$ $g^{-1}$, 0.129 $cm^3$ $g^{-1}$ and 2.95 nm, respectively. Given the surface properties of the modified catalyst, it could serve as a good choice for the biodiesel production.

### Impact of Methanol-to-oil Ratio on Biodiesel Production

In the transesterification reaction, the methanol-to-oil ratio acts as a key parameter affecting the performance of the methyl ester as well as the biodiesel production cost [2]. A lower molar ratio of the alcohol to oil affects the triglyceride to methyl ester conversion efficiency [15]. Results of the effect of the methanol-to-oil ratio on the biodiesel conversion efficiency are shown in Fig. 3. As shown on the figure, with increasing the methanol-to-oil ratio, the biodiesel conversion efficiency increased initially to a maximum value at the methanol-to-oil ratio of 1:15. However, any further increase in the methanol-to-oil ratio up to 1:18 lowered the biodiesel efficiency. Accordingly, the methanol-to-oil ratio of 1:15 was used for the rest of experiments. This outcome could be attributed to the fact that the increase in the methanol content of the mixture facilitated the dissolution of the glycerin and alcohol in the biodiesel, significantly influencing its purity.

### Impact of the Catalyst Dosage

The catalyst dosage affects the biodiesel generation. The catalyst dosage imposes large contributions to the rate of reaction. In general, the more active a catalyst is, the lower is the applied dosage of the catalyst [6]. Results of
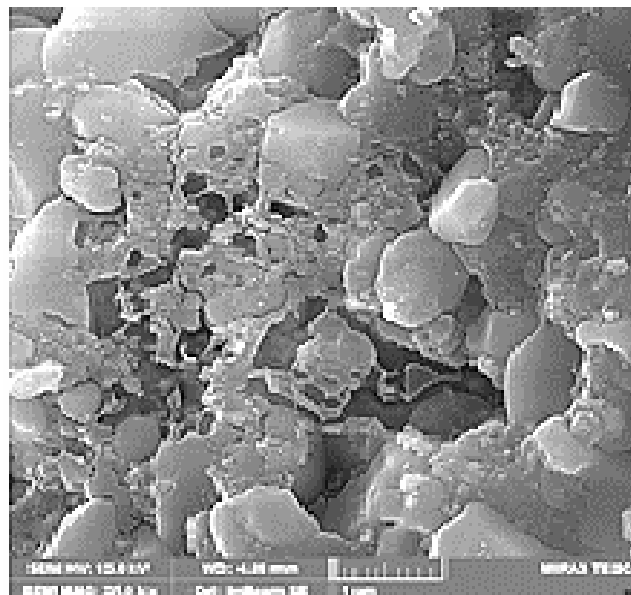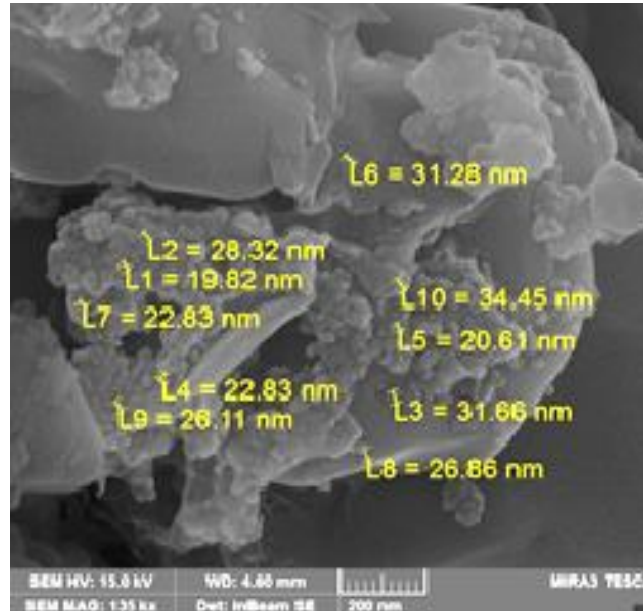
**Fig. 1.** SEM image of the CaO catalyst at different scales.

evaluating the effect of catalyst dosage on the biodiesel generation are presented in Fig. 4. As is evident from the figure, the biodiesel generation followed an initially increasing trend with increasing the catalyst dosage, so that the maximum biodiesel conversion efficiency was achieved at a catalyst dosage of 1.5 wt.%. At higher dosages of the catalyst, however, the biodiesel efficiency declined, seemingly because of the increased viscosity of the reaction mixture upon excessive use of the catalyst that made the mixing problematic and thus lowered the oil-to-biodiesel conversion efficiency [15]. Accordingly, a catalyst dosage of 1.5 wt.% was considered as the optimal catalyst dosage.
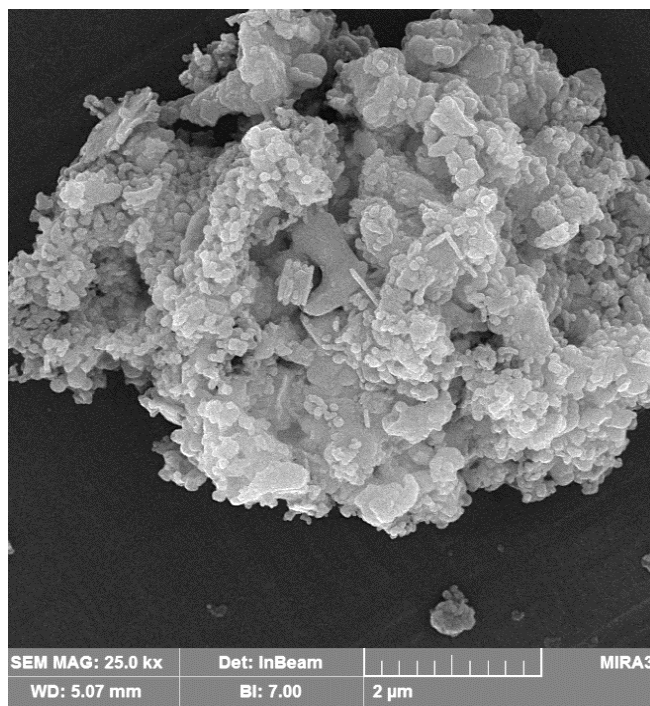
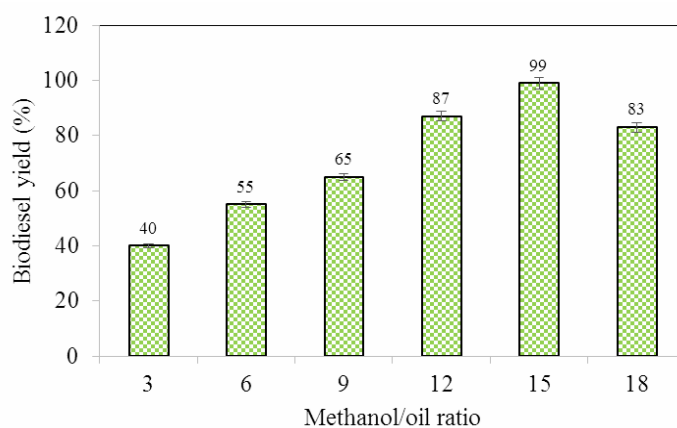**Fig. 2.** SEM image of the KOH-impregnated CaO catalyst.



**Fig. 3.** Impact of the methanol/oil ratio on the biodiesel production efficiency (reaction temperature: 65 °C, catalyst dosage: 1.5 wt.%, reaction time: 4 h).

**Impact of Temperature**

The impact of temperature on the rate of chemical reactions is so strong, because the reaction rate is, according to the Arrhenius equation, dependent to the temperature [16]. The transesterification of the herbal oils with methanol is performed in liquid phase. Accordingly, the reaction temperature may not exceed the boiling point of the methanol (65 °C under atmospheric pressure) [10]. The
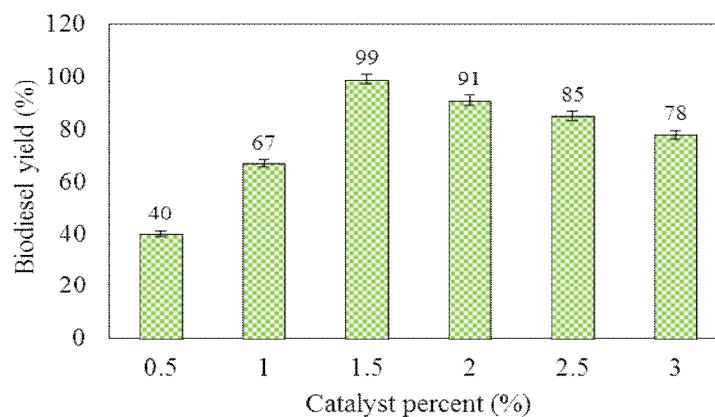
**Fig. 4.** Effect of the catalyst dosage on the biodiesel production efficiency (methanol-to-oil ratio: 1:15, reaction temperature: 65 °C, reaction time: 4 h).
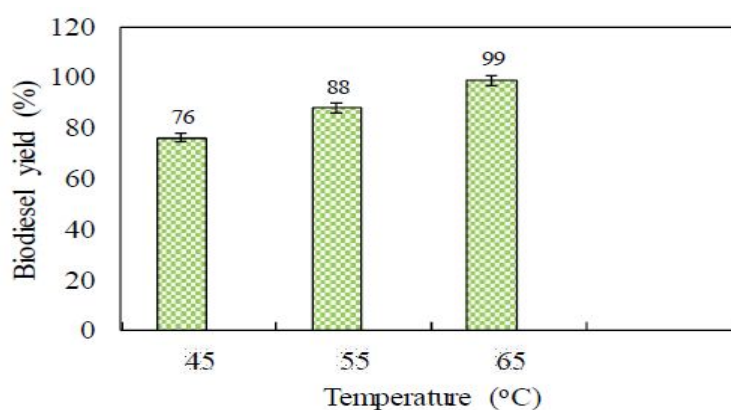


**Fig. 5.** Effect of temperature on the biodiesel production efficiency (methanol-to-oil ratio: 1:15, reaction time: 4 h, catalyst dosage: 1.5 wt.%).

effect of this parameter is demonstrated in Fig. 5. Investigation of this figure shows that the biodiesel efficiency increased with temperature up to 65 °C where the highest biodiesel production efficiency was achieved. Accordingly, the rest of experiments were performed at 65 °C.

**Impact of Reaction Time**

The reaction time is another important factor affecting the biodiesel generation, with the effect depended on the catalyst type [9]. Results of evaluating the impact of reaction time on biodiesel yield are shown in Fig. 6. The

outcomes highlight the fact that the biodiesel production efficiency increased with the reaction time up to 4 h when the maximum yield of conversion was obtained. After the optimum reaction time of 4 h, the biodiesel production efficiency decreased due to the occurrence of the reverse reaction. That is attributable to the reversible nature of the transesterification of the herbal oils with methanol, as was previously reported by Chen *et al.* [17]. Therefore, the optimal reaction time was found to be 4 h.

**Comparison to other Works**

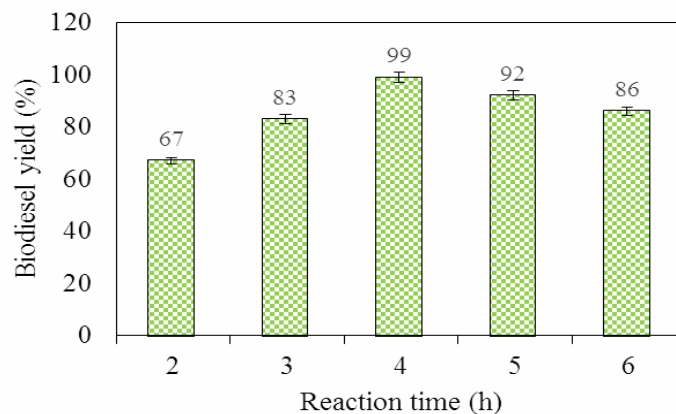In this study, biodiesel production from the olive oil was

**Fig. 6.** Effect of the reaction time on the biodiesel production efficiency (methanol-to-oil ratio: 1:15, temperature: 65 °C, catalyst dosage: 1.5 wt.%).

**Table 3.** Comparison of the Catalyst Developed in this Work Against other Catalysts Used for the Biodiesel Production from the Olive Oil in other Works

| Catalyst | Methanol/oil ratio | Contact time (min) | Temperature (°C) | Catalyst content (%) | Biodiesel yield (%) | Ref. |
|---|---|---|---|---|---|---|
| SrO/SiO$_2$ | 6:1 | 20 | 55 | 5 | 95 | [17] |
| SrO/CaO | 6:1 | 40 | 55 | 5 | 95 | [17] |
| SrO | 6:1 | 15 | 65 | 5 | 82 | [17] |
| clinoptilolite | 7:1 | 180 | 65 | 3 | 92 | [18] |
| ZnO nanorods | 15:1 | 480 | 150 | 1 | 94.8 | [19] |
| nano tube TiO$_2$ | 10:1 | 240 | 120 | 4 | 91.2 | [20] |
| NaOH | 4:1 | 240 | 50 | 4 | 76.4 | [21] |
| NaOH | 6:1 | 80 | 60 | 1 | 95 | [22] |
| Zinc stearate | 20:1 | 30 | 140 | 3 | 84.1 | [23] |
| CaO@KOH | 15:1 | 240 | 65 | 1.5 | 99 | Present study |

practiced in presence of CaO@KOH catalyst, and the outcomes were compared to the biodiesel production from the olive oil in presence of other catalysts (Table 3). As is evident from the table, the biodiesel production efficiency was much higher with the catalyst synthesized in this study rather than those reported in the previous works, proving high performance of the developed catalyst.

**Reusability of the CaO@KOH Catalyst**

The reusability of the catalyst plays a crucial role in the

economic efficiency of the transesterification reaction and hence the biodiesel production process. In order to evaluate the reusability of the developed catalyst, it was successively reused under the optimum conditions (methanol-to-oil ratio: 1:15, reaction temperature: 65 °C, catalyst dosage: 1.5 wt.%, reaction time: 4 h). After each transesterification cycle for the biodiesel production, the catalyst was separated by vacuum filtration, washed by methanol and then dried by the oven at 100 °C. This regeneration procedure was repeated for each cycle. In this work, the developed catalyst was reused for biodiesel production for a total of 8 cycles, the outcomes are demonstrated in Fig. 7. According to the figure, the biodiesel conversion efficiency suffered from only subtle changes after 4 cycles, indicating the great reusability of the catalyst for the biodiesel production. Moreover, after 7 cycles of reuse, the biodiesel production efficiency remained above 90%, indicating that the catalyst could be reused for biodiesel production for up to 7 cycles, highlighting the economic advantage of the catalyst.

**Evaluation of Physical Properties of the Biodiesel**

The physical properties of the produced biodiesel and its blends with conventional diesel at different blending ratios (designated as B25, B50, B75 and B100), including the density, the viscosity, the flash point, the cloud point, and the pour point, were measured and are reported in Table 4.

Affecting the atomization efficiency of the fuel, the density is an important parameter of any fuel [8]. The relative density of the produced fuel plays a critical role in the injected amount of fuel by a fuel injection system. Accordingly, when the fuel density is high, the transmitted amount of fuel by the fuel injection system would be very small [7]. According to EN14214 standard code, the allowable range of density for a diesel fuel is 860-900 kg m$^{-3}$. Based on Table 4, the biodiesel and pure diesel had density values of 882.6 and 837.9 kg m$^{-3}$, respectively, showing that the produced biodiesel had a density in the standard range while the diesel was out of range. Considering different blends, the B50, B5 and B100 exhibited appropriate densities based on the standard code.

As a critical property of a fuel, the kinematic viscosity plays an important role in the fuel spraying efficiency, fuel mixing efficiency and burnability of the fuel [9]. In a fuel

delivery system, the fuel viscosity affects the lubrication of the system. Accordingly, a too low viscosity keeps the fuel from lubricating the injection system adequately and hence accelerates the system fatigue and leakage problems. On the other hand, if the fuel viscosity is too high, the fuel injection system will require excessive energy to spray the fuel, inhibiting appropriate dispersion of the fuel and hence the released energy while adding to the generated suspended particles and exhaust gases [24]. According to Table 4, the viscosity of the produced biodiesel was measured at 5.4699 mm$^2$ s$^{-1}$, falling in the allowable range by the ASTM D6751 standard code and being larger than that of the fuel diesel (2.2907 mm$^2$ s$^{-1}$). Therefore, it could be concluded that the produced biodiesel could provide the system with more lubricating effect, thereby preventing the corrosion of the system. However, as discussed above, excessively high viscosity of the fuel lowers the fuel delivery and adds to the required energy for fuel injection. In this respect, the viscosity of the pure gasoil was better than that of the produced biodiesel as it lowered the required energy for injecting the fuel into the system.

The flash point refers to the lowest temperature at which a combustible blend can be obtained from the liquid fuel. This is a very important parameter for fuel storage and safety [6]. Based on the outcomes tabulated in Table 4, the flash points of the B25, B50 and B75 blends were dominantly determined by the flash point of the fuel diesel, making them out of the allowable range set by the mentioned standard code. Moreover, the flash point of the produced biodiesel (178 °C) was significantly higher than that of the fuel diesel (66 °C), making it preferable over the diesel in terms of safety and storage requirements.

Performance of the biodiesel at lower temperatures is usually determined by its cloud and pour points. The cloud point has been defined as the temperature at which the smallest cluster of the crystalline wax appears for the first time [6]. By definition, the pour point is the temperature at which the fuel takes a semi-solid form, losing its flowing character; in this respect it is also known as the gelation point of the fuel. The pour point is always lower than the cloud point and independent of the catalyst type or other reaction parameters. For the biodiesel, the pour point has contributions from the FA content of the source oil [2]. The set of ASTM and EN standard codes have defined no
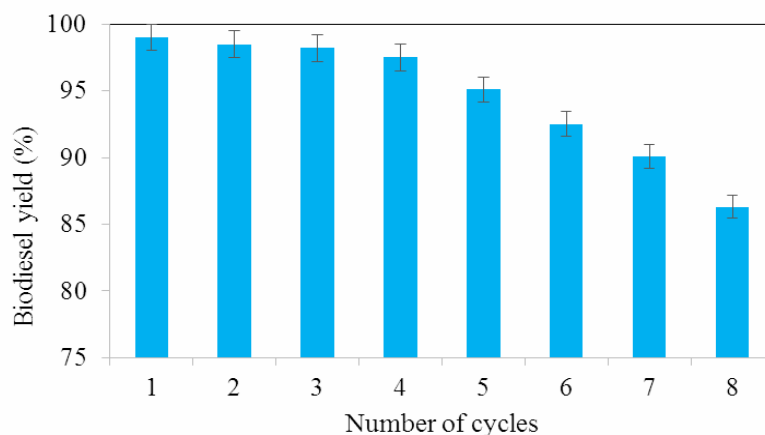
**Fig. 7.** Reusability of the CaO@KOH catalyst for producing biodiesel from olive oil (conditions: methanol/oil ratio: 1:15, temperature: 65 °C, catalyst dosage: 1.5 wt.%, time: 4 h).

**Table 4.** Physical Properties of the Produced Biodiesel and its Blends with Conventional Diesel at Ddifferent Blending Ratios

| Analysis | Standard | Range | B100 | B75 | B50 | B25 | B00 |
|---|---|---|---|---|---|---|---|
| Density at 15 °C ($kg\ m^{-3}$) | EN14214 | 860-900 | 882.6 | 870.8 | 860.1 | 851.5 | 837.9 |
| Kinematic viscosity at 40 °C ($mm^2\ s^{-1}$) | ASTM D6751 | 2-6 | 5.47 | 3.76 | 3.68 | 3.10 | 2.96 |
| Flash point (°C) | ASTM D6751 | >130 | 178 | 91 | 80 | 72 | 66 |
| Cloud point (°C) | - | - | 6 | 4 | 2 | 0 | -2 |
| Pour point (°C) | - | - | -5 | -7 | -10 | -12 | -15 |

allowable ranges for neither the cloud point nor the pour point, so that one must specify such ranges depending on the local climate. In the present investigation, the produced biodiesel exhibited a cloud point of 6 °C while the diesel had a cloud point of -4 °C. This finding showed that the produced biodiesel was not an appropriate choice for too cold areas. Moreover, the pour point of the produced biodiesel was found to be -5 °C, which was a good value

compared to similar biodiesels, but still kept us distance from recommending the biodiesel for cold areas where the temperature frequently falls below the pour point. Considering the obtained values of the cloud and pour points for the produced biodiesel and the diesel, it was evident that the larger the fraction of the diesel in the diesel-biodiesel blend, the lower would be the obtained pour point. In this respect, the low-biodiesel blends could be appropriately recommended for cold areas.

## CONCLUSIONS

In the present work, the olive oil and methanol were used for biodiesel production. In order to accelerate the transesterification reaction, a composite CaO@KOH catalyst was used, both constituents were alkali. The catalyst was characterized by performing SEM and BET analyses. Next, in order to maximize the biodiesel production efficiency, effects of different parameters (temperature, reaction time, catalyst dosage, and methanol-to-oil ratio) on the biodiesel production efficiency were evaluated. The outcomes indicated that the maximum efficiency (99%) could be obtained at a methanol-to-oil ratio of 1:15, a catalyst dosage of 1.5 wt.%, a reaction temperature of 65 °C, and a reaction time of 4 h. Once the biodiesel was produced under optimum conditions, its physical properties including the density, the viscosity, the flash point, the cloud point, and the pour point were evaluated and compared to those of blends with gasoil at different blending ratios (designated as B25, B50, B75 and B100) as well as the allowable ranges mentioned in the ASTM D6751 and EN14214 standard codes. The outcomes indicated that all properties of the produced biodiesel were in the allowable ranges set by the standard codes, indicating that the produced biodiesel was a good alternative to the diesel. Moreover, reusability of the catalyst was evaluated by its reuse through 8 successive cycles, with the outcomes confirming the large potentials of the catalyst for the biodiesel production, making it economically much affordable.

### Conflict of Interest Statement
The authors declare that there is no conflict of interest.

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