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Optimization of Biodiesel Production from Sunflower Oil Transesterification using Ca-K/Al$_2$O$_3$ Nanocatalysts

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A B S T R A C T

In this study, an attempt was made to optimize the conditions for the transesterification of sunflower oil with methanol, catalyzed by Ca-K/Al$_2$O$_3$ nanocatalysts, using response surface methodology. The examined variables were reaction temperature (55, 65 and 75 °C), reaction time (1, 2, 3, 4 and 5 h), catalyst weight base oil (3, 6, 9 and 12 wt%), Ca content (20, 30, 50, 60 and 80 wt%), K content (5, 10, 15 and 20), methanol:sunflower oil molar ratio (3:1, 6:1, 9:1 and 12:1), calcination temperature (600, 700 and 800 °C) and calcination time (1, 2, 3 and 4 h). Catalyst characterization was done by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform-infrared spectroscopy (FT-IR) and temperature programmed desorption (TPD). The maximum fatty acid methyl esters (FAME) conversion efficiency (biodiesel production efficiency) was 98.3%, at a calcination temperature of 800 °C for 3 h, a methanol-to-oil ratio of 9:1, a reaction temperature of 75 °C, a reaction time of 3 h and a catalyst-to-oil mass ratio of 9%.

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1. INTRODUCTION

The increasing demand for energy, the rising price of crude oil, global warming resulting from the emission of greenhouse gases, environmental pollution and the rapidly decreasing supply of fossil fuels are the key factors motivating the search for alternative energy sources. Some of the most significant alternative sources of energy that have the ability to replace fossil fuels are hydropower, solar and wind energy, and biofuels. Today, 86% of the energy consumed worldwide, as well as nearly 100% of energy demanded in the transportation sector, is produced using non-renewable fossil fuels despite the various alternative fuels that are being explored to replace existing fossil diesel [1].

Biodiesel is a fuel comprised of mono-alkyl esters of fatty acids derived from animal fats or vegetable oils. It reveals diesel quality and is identified as a clean and renewable fuel [2]. In recent years, many researchers have paid a lot of attention to biodiesel development due to the rate of fossil fuel depletion and because of the resemblance of biodiesel to diesel based on petroleum [3, 4]. Biodiesel can also be used in diesel engines without any engine modifications. Biodiesel is produced through triglyceride transesterification using alcohol in the presence of a catalyst or through deoxygenative ecofining of triglycerides in a non-alcohol situation [5].

Biodiesel can be produced using a wide variety of feedstocks. These feedstocks can be broken up into two categories, unrefined oils and waste oils [6]. Unrefined
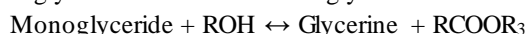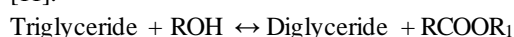
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oils are further divided into edible and non-edible oil sources [7]. Edible oil feedstocks include soybean, sunflower, peanut, rapeseed (canola), and coconut oils. Nonedible feedstocks are less widely talked about than edible oils. Non-edible oil sources include jatropha, pongamia, argemone, and castor oils. The advantages of using unrefined oil include low levels of impurities and known lipid composition. The main disadvantage of virgin oils is the high cost [8].

Waste oil often comes from the same sources originally. It has just been used, for example in cooking, before being converted into biodiesel. Waste oils can also come from other sources such as animal fat from slaughterhouses [9]. Waste oils are a good feedstock for personal biodiesel production, people making biodiesel in small batches in their garage, because the waste oil can be obtained very cheaply or even for free from restaurants needing to dispose of used frying oil. However, due to the fact that oil has already been used, there are higher amount of animal fats and other contaminants in the oil [6].

There are four primary ways to produce biodiesel, namely, direct use and mixing of raw oils, microemulsions, thermal cracking and transesterification. The most commonly used method of biodiesel production is transesterification (also identified as alcoholysis) in the presence of a catalyst. The process of substituting the alkoxy group of an ester compound with another alcohol is called transesterification [10].

Fatty acid chains are long hydrocarbon chains, and include R1, R2 and R3 [11]. Transesterification involves a series of successive, reversible reactions [12, 13]. The triglyceride is transformed stepwise into diglyceride, monoglyceride and, finally, glycerol by reacting with preliminary alcohol, as illustrated in following reactions [11]:

Triglyceride + ROH ↔ Diglyceride + $RCOOR_1$

Diglyceride + ROH ↔ Monoglyceride + $RCOOR_2$

Monoglyceride + ROH ↔ Glycerine + $RCOOR_3$

Methanol and ethanol are two types of alcohol (R-OH) that are commonly applied in transesterification, but methanol is the most popular considering its low cost, low reaction temperatures, fast reaction times and high quality methyl ester products [14, 15]. The transesterification of unrefined oils and waste oils to biodiesel with methanol can be accomplished by applying both homogeneous (acid or base) and heterogeneous (acid, base and enzymatic) catalysts [16].

Base catalyst transesterification is extensively applied commercially due to its very rapid reaction rate in contrast to other catalysts. A base-catalyzed process is very permeable to water and free fatty acids (FFA) in lipid sources because of the formation of soap. It causes catalyst utilization in which soap production hinders the separation of glycerol from methyl esters and helps emulsion formation through the water wash. The base-catalyzed transesterification is 4000 times faster than acid-catalyzed transterification and requires a low triglyceride-to-alcohol ratio [17].

Heterogeneous catalysts, compared to homogeneous catalysts, are environmentally benign and can be operated in consecutive processes. In addition, they can be reapplied and reproduced. Thus, heterogeneous catalysts are now being examined widely for biodiesel synthesis [18, 19]. It should be noted that solid bases are more active than metal compounds and need milder reaction situations than acids [20, 21].

Experimental design is a strategy for collecting empirical knowledge that relies on experimental data analysis and not theoretical models. The objective of experimental design is to attain efficiency (to obtain more information from fewer experiments) and focus (to gather only the information you really require) [22, 23]. Central composite design is the most common design of response surface methodology (RSM); it is efficient and flexible, providing sufficient data on the effects of variables and overall experimental error with a minimum number of experiments [24, 25].

In this study, the effects of eight independent numerical factors, namely, calcination temperature, calcination time, temperature of transesterification, time of transesterification, weight ratio of methanol to oil, weight ratio of catalyst to oil and weight ratio of potassium and calcium were examined. Characterization of catalysts was conducted by X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform-infrared spectroscopy (FT-IR) and temperature programmed desorption (TPD).

2. MATERIALS AND METHODS

2. 1. Materials KNO_3, Al_2O_3 Na_2CO_3, ethanol (98%) and Ca $(NO_3)_2.4H_2O$ were supplied by Merck (Darmstadt, Germany). Materials for refining sunflower oil were prepared from a local grocery store. The triglyceride and fatty acid values in the sunflower oil were specified by gas chromatography. The fatty acid values were as follows: palmitic acid 7.68%, stearic acid 3.1%, oleic acid 19.95% and linoleic acid 65.95%. The acid value, the water content, the viscosity and the density of the oil were specified according to the current European Union Quality Standard (EN-14214). These values are summarized in Table 1.

TABLE 1. Sunflower oil properties

Property	Value
Acid value (%)	0.1
Water content (%)	0.1
Viscosity at 40°C (cSt)	29.6
Density at 40°C (g/cm³)	0.924

2. 2. Preparation of the Ca-K/Al₂O₃ Nanocatalyst

Based on coprecipitating $Ca(NO_3)_2.4H_2O$ and KNO_3, a Ca/K oxide catalyst was prepared and Na_2CO_3 was applied as a precipitant. A sequence of catalysts with various Ca/K molar ratios was prepared by dissolving defined values of $Ca(NO_3)_2.4H_2O$ and KNO_3 in deionized water and by adding an aqueous Na_2CO_3 solution under vigirous stirring at room temperature until the pH became fixed [26, 27].

The catalyst preparation was performed in a three-neck round-bottom flask (250 mL) equipped with a reflux condenser, a temperature indicator and a mechanical stirrer. Al_2O_3 was added into the three-neck round-bottom flask as a supporter. The impregnation of $Ca(NO_3)_2.4H_2O$ with KNO_3 at a temperature of 65°C for 3 h under continuous stirring was performed. On completion of the impregnation process, the slurry was dried in an oven at 80°C for 12 h to eliminate water. Thereafter, the catalyst was calcined in a tubular muffle furnace at a temperature of 800°C for 3 h.

2. 3. Catalyst Characterization

The prepared catalysts were characterized using several methods, such as XRD, FT-IR, TPD and SEM. Calcined samples and the XRD patterns of all the precursors were registered on a Philips X' Pert (40 kV, 30 mA) X-ray diffract meter, applying a Cu Kα radiation source (λ=1.542 Å) and a nickel filter in the 2θ range of 20–80°. SEM analysis was applied to specify morphology, aggregate particles, grain boundaries and defects. The surface morphologies were observed and estimated by a Philips XL30 microscope at a rising voltage of 10 kV. The fourier transform infrared (FT-IR) spectra of the samples in the form of KBr pellets were recorded using a Bruker FT-IR in the area of 400–4000 cm^{-1}. Temperature programmed desorption (TPD) in the presence of H_2 gas was performed from 200 to 1100 K for measuring of H_2 consumption with a linear heating rate of 10°C/min in 5% H_2 per 95% Ar [27].

2. 4. Sunflower Oil Transesterification

The transesterification of 15 g waste sunflower oil was performed using a 250 mL round-bottomed flask equipped with a magnetic stirring system (reaction system) and a condenser. First, the reaction system was heated to reach the desired temperature while the oil reached the desired temperature; then, the catalyst and the methanol were added with continuous stirring (500 rpm). The catalytic solid was separated from the reaction combination by applying an external magnetic field on fulfilment of the reaction. The products obtained were evaporated to eliminate additional methanol and then fixed in a separating funnel. The upper phase was composed of fatty acid methyl esters (biodiesel) and the lower phase consisted of glycerol as a byproduct. Minitab.16 software based on RSM was used in this study. For each system, 13 experiments were designed

based on two variables. The experimental range and the levels of the independent variables are indicated in Table 2. Weight ratio of methanol to oil (A, w/w %) ranged from 3:1 to 18:1 at 5 levels (3:1, 6:1, 9:1, 12:1 and 18:1); weight ratio of catalyst to oil (B, w/w %) ranged from 3 to 12% at 4 levels (3, 6, 9 and 12); weight ratio of calcium (C, wt. %) ranged from 20 to 80% at 5 levels (20, 30, 50, 60 and 80%); weight ratio of potassium (D, wt. %) ranged from 5 to 20% at 4 levels (5, 10, 15 and 20 %); calcination temperature (E, °C) ranged from 600 to 800 °C at 3 levels (600, 700 and 800 °C); calcination time (F, h) ranged from 1 to 4 h at 4 levels (1, 2, 3 and 4 h); time of transesterification (G, h) ranged from 1 to 5 h at 5 levels (1, 2, 3, 4 and 5 h); temperature of transesterification (H, °C) ranged from 55 to 75 °C at 3 levels (55, 65 and 75 °C).

Based on the values of the variables that were studied and the responses obtained after the transesterification process, the viscosity was evaluated and the yield of biodiesel was calculated. The applied data for the software were uncoded and the real data were considered. Equation (1) was obtained for each system. A group of coefficients was presented for each series and the most effective coefficient was considered in the response. In this research, the experiments had two variables; this equation included two X values. The number of X was increased by increasing the number of variables, as follows:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_{12} + \beta_{22} X_{22} + \beta_{12} X_1 \tag{1}$$

The impact on the yield increased along with an increase in the value of coefficients. The impact on the response was raised by raising the value of the F parameter and reducing the P parameter.

3. RESULTS AND DISCUSSION

3. 1. Catalyst Characterization Figure 1 indicates FT-IR spectra of the Ca-K/Al₂O₃ nanocatalyst. The stronger broadening band at 3400 cm^{-1} can be attributed to the hydrogen bond between the different hydroxyl groups in the product. The intense expansive band at 1630 and 1078 cm^{-1} is related to Al-O vibration [17]. The bands at 3644 and 1420 cm^{-1} correspond to K_2O/CaO [18]. The intense characteristics of IR spectral lines for

TABLE 2. Experimental range and levels of the independent variables

Variables	A	B	C	D	E	F	G	H
Levels	5	4	5	4	3	4	5	3
Min	3:1	3%	20	5	600	1	1	55
Max	18:1	12%	80	20	800	4	5	75

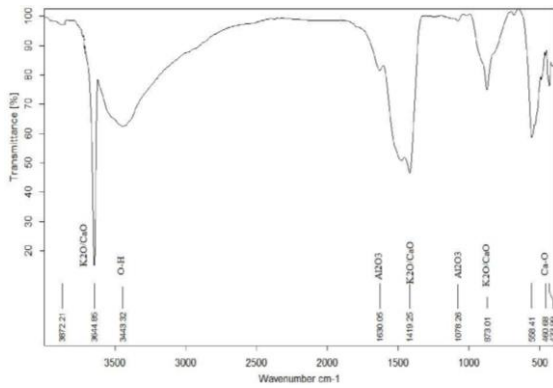**Figure 1.** FT-IR spectra of Ca-K/Al$_2$O$_3$ nanocatalyst

Figure 3. SEM of Ca-K/Al$_2$O$_3$ nanocatalyst

CaO occur in the far-infrared range (~480 cm^{-1} and 433 cm^{-1}) and one weak band is placed in the range of 500 cm^{-1} to 560 cm^{-1} [19].

X-ray diffraction was confirmed for the Ca-K/Al$_2$O$_3$ catalyst, as shown in Figure 2. The results obtained indicated the recognized phases for this sample. The recognized phases for the calcined Ca-K/Al$_2$O$_3$ catalyst were Al$_2$O$_3$ ((hexagonal), K$_2$O (cubic) and CaO (cubic). The particle size of catalyst could be calculated 33.64 nm by Scherer equation [20]. As shown in Figure 3, the surface morphology of the Ca-K/Al$_2$O$_3$ nanocatalyst was investigated with SEM image. As can be seen in Figure 3, the Ca/K oxide catalyst is successfully deposited on Al$_2$O$_3$ surface.

Characterization of the basic property of catalyst Ca-K/Al$_2$O$_3$ nanocatalyst was investigated as displayed in Figure 4. Usually, two desorption peaks were observed in the TPD profile, as shown in Figure 4; these are in the low and high temperatures of desorption. The strength of basic sites was deduced from the work by Pasupulety et al. [21], where it was suggested that desorption temperature between 330-620 °C indicates basic sites of weak and medium strength, and desorption temperature range of 770-980 °C indicates strong basic sites. The peak at 850 °C is desorption of CO$_2$ which was adsorbed on the basic sites [21].
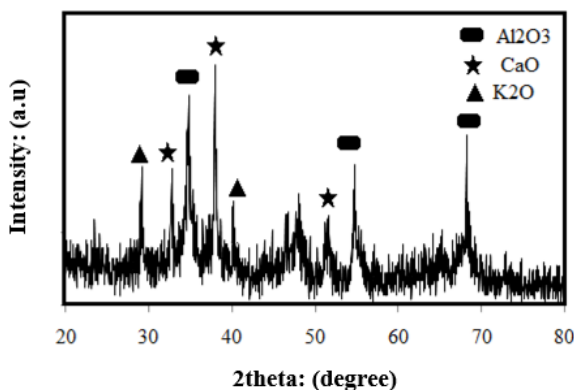
The total amount of CO$_2$ desorbed for a Ca-K/Al$_2$O$_3$ nanocatalyst is equal to 1.42×10^{21} (atom g^{-1}). The high basic sites of the catalyst bring about high-yield biodiesel. Regarding the relationship between transesterification and the surface basicity of a La$_2$O$_3$/ZrO$_2$ catalyst, Sun et al. argue [22] that a correlation between basic properties occurs when the catalytic reaction is activated, so that a higher biodiesel yield is attained with stronger basicity.

3. 2. Effect of Molar Ratio of Methanol and Mass Ratio of Catalyst to Oil   Table 3 indicates the experimental results at various mole ratios of methanol and mass ratios of catalyst to oil. This reaction stoichiometry needs 3 mol methanol per mol triglyceride to produce 3 mol biodiesel and 1 mol glycerol. The biodiesel is increased in an additional amount of methanol to shift the balance toward the right-hand side [28]. To completely understand the factors that affect the catalytic performance of the optimal Ca-K/Al$_2$O$_3$ catalyst, many experiments were performed at various methanol:oil ratios, ranging from 3:1 to 18:1, under the reaction situations (T=75°C, stirring rate of 500 rpm and reaction time of 3 h). The table indicates that the biodiesel yield percent considerably increased in methanol oil ratio =9:1. Thus, it can be said that increasing the methanol value postponed the reaction and exacerbated the solvent recovery. However, recovering solvent with a high ratio
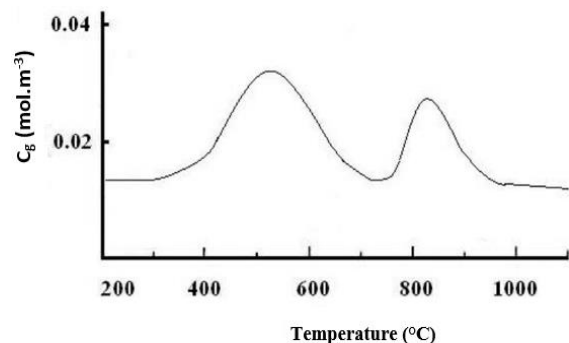

Figure 2. X-ray diffraction of Ca-K/Al$_2$O$_3$ nanocatalyst

Figure 4. TPD of Ca-K/Al$_2$O$_3$ nanocatalyst

TABLE 3. The effect of methanol:oil ratio and catalyst:oil ratio on biodiesel yield

Methanol to oil (w/w %)	Catalyst to oil (w/w %)	Viscosity (cp)	Yield (%)
3	6	10.53	33.70
12	6	3.18	99.29
12	6	3.18	99.29
12	3	5.04	75.48
12	12	3.73	91.59
12	6	3.18	99.29
9	6	4.39	83.15
18	6	3.18	99.23
3	3	11.62	28.68
18	3	3.29	97.70
3	12	10.53	33.70
12	6	3.18	99.29
9	9	3.14	99.89

of methanol to oil was very difficult, and emulsification could take place in washing products. A catalyst possessing powerful basic locations and a big surface area should indicate high activity. In this research, the mass ratio of Ca-K/Al$_2$O$_3$ to sunflower oil differed within a range of 3–12%. According to the results obtained, as set out in Table 3, the biodiesel yield percent significantly increased in catalyst oil ratio =9:1.

A model presented by DoE software was fitted with the actual data presented in Equation (2) to describe the effect of the variables examined.

$$\text{Yield} = 49.1140 + 14.5286A + 9.1274B - 0.4111A^2 - 0.3837B^2 - 0.1844AB \qquad (2)$$

The ANOVA results on the effect of the variables are summarized in Table 4, where A is the methanol-to-oil ratio and B is the weight fraction of the catalyst (%). The impact on the biodiesel yield was more considerable when the value of coefficients was increased [23]. The impact on the response was raised by raising the value of the F parameter and reducing the P parameter. As can be seen, the remarkable parameters of reaction were included (most to least significant) [24]: methanol-to-oil ratio (14.52) > weight fraction of the catalyst (9.12) > second-order effect of methanol-to-oil ratio (− 0.41) > second-order effect of the weight fraction of the catalyst (− 0.38) > interaction between methanol-to-oil ratio and weight fraction of the catalyst (- 0.18). The F value and the P value were applied to measure the significance of the coefficients (see Table 4). The negative effects of quadratic terms on biodiesel yield in the polynomial expression were shown by their negative coefficients. This result can be related to the experimental range of

independent variables selected in this research. The F value and the P value indicated the significance of the coefficients (see Table 4).

The correlation coefficient square for each response was calculated as the coefficient of determination (R^2). The R^2 coefficient presents the proportion of the total response variation forecasted by the model, representing the ratio of squares due to regression (SSR) to total sum of squares (SST). The coefficient of determination R^2 can be examined by the accuracy and variability of the model. It is always between 0 and 1, and when the R^2 value is closer to 1, the model is stronger and predicts the response better [25, 29]. An R^2 value of 0.9 relatively ensures a desirable adjustment of the model to the experimental data.

3. 3. Effect of Reaction Temperature and Reaction Time   The experimental findings at various reaction temperatures and times are indicated in Table 5. Reaction temperature can affect the reaction rate as well as biodiesel yield. In this research, the reaction temperature differed within a range of 55–75°C. At low temperatures, the rate of reaction was slow and the biodiesel yield was only 31.59% at 55°C after 60 min.

The biodiesel yield increased with a rise in reaction temperature to approximately 99.7% at 75°C. A shorter reaction time is a preliminary benefit of a higher temperature; however, if the reaction temperature were to be above the boiling point of methanol (64.7°C), the methanol would vaporize and form many bubbles, which would prevent the reaction on the three-phase interface. In the setup applied in this research, a system with a high-performance condenser was applied to prevent high temperature inhibition. Thus, the optimized reaction temperature for sunflower oil transesterification to biodiesel is about 75°C.

Overall, the lipid transformation rate increased as the reaction time increased. At the reaction start, the speed was very low due to the need to combine and distribute alcohol into the oil. After this step for vegetable oil, 80% of the transesterification reaction could be completed in a short period and almost completed in another hour. However, the lipid conversion rate remained relatively

TABLE 4. ANOVA results on the effect of methanol:oil ratio and catalyst:oil ratio

Term	Coefficient (ß)	F value	P value
Constant	-49.114	-	-
A	14.5286	15.30	0.006
B	9.1274	1.87	0.214
A^2	-0.4111	7.53	0.029
B^2	-0.3837	0.68	0.436
AB	-0.1844	0..44	0.529

TABLE 5. The effect of reaction temperature and reaction time on biodiesel yield

Reaction time (h)	Reaction temperature (°C)	Viscosity (cp)	Yield (%)
3	65	6.58	60.22
3	65	6.58	60.22
3	65	6.58	60.22
3	65	6.58	60.22
3	75	3.07	99.70
1	75	9.43	39.59
1	65	10.31	34.80
1	55	10.96	31.59
5	55	8.55	45.05
5	65	3.51	94.60
3	55	9.87	37.12
3	65	6.58	60.22
5	75	3.29	97.70

stable with a further rise in reaction time [17]. In addition, more reaction time resulted in a reduction in product yield because the reversible transesterification lead to ester loss and more fatty acids for soap formation.

Many tests were carried out to investigate the function of the optimum Ca-K/Al$_2$O$_3$ catalyst at different reaction times within the range of 1–5 h, at the optimized reaction situations (methanol:oil=9:1, catalyst:oil=9:1, T=75°C and stirring rate of 500 rpm). The biodiesel yield percent slightly increased with an increase in reaction time. Thus, a reaction time of 3 h for biodiesel production seemed optimal. Owing to increased contact time between reactants, enhancing the reaction time enhances the biodiesel yield, whereas enhancing the reaction time further has no remarkable impact on the biodiesel yield since the balance situation is almost completed [30].

A model presented by DoE software was fitted with the actual data presented in Equation (3) to describe the effect of the variables examined.

$$\text{Yield} = 77.1881 - 12.9134G - 2.5822H - 2.0756G^2 + 0.0248H^2 + 0.5452HG \tag{3}$$

The ANOVA results regarding biodiesel yield are summarized in Table 6, where G is reaction time and H is reaction temperature. Reaction time and interaction between reaction time and reaction temperature were chosen as the effective terms with higher coefficient values than other variables. The F value and the P value specified the significance of the coefficients (see Table 6). The square of the correlation coefficient for every response was measured as the coefficient of determination (R^2). A value of 0.84 for R^2 indicates that

some other variables might have interacted on the response, but those variables were not considered in this study.

3. 4. Effect of Weight Fraction of Calcium and Potassium   The weight fraction of calcium and potassium can affect the biodiesel product yield, which indicates the relationship of the weight fraction of calcium and potassium with the rate of lipid conversion. With reference to Table 7, when the concentration of potassium was 15% and the concentration of calcium was 20%, the highest lipid conversion rate (97.41%) was obtained. The lipid conversion rate (37.12%) decreased sharply when the concentration of potassium was 20% and the concentration of calcium was 60% and it continued to decrease as the weight fraction of calcium and potassium increased. Increasing the weight fraction of calcium and potassium leads to the production of more soap, which consumes the catalyst and decreases the catalytic efficiency [31].

TABLE 6. ANOVA results on the effect of reaction temperature and reaction time

Source	Coefficient (ß)	F value	P value
Constant	77.1881	-	-
G	-12.9134	0.23	0.644
H	-2.5822	0.06	0.814
G^2	-2.0756	0.91	0.372
H^2	0.0248	0.09	0.769
HG	0.5452	2.46	0.161

TABLE 7. The effects of calcium and potassium weight fraction on biodiesel yield

Ca (%)	K (%)	Viscosity (cp)	Yield (%)
50	10	3.96	88.43
50	5	3.93	88.92
50	15	7.99	48.94
60	20	9.87	37.12
50	10	3.96	88.43
20	15	3.30	97.41
80	5	4.03	87.61
80	20	5.43	71.27
50	10	3.96	88.43
60	15	3.75	91.33
20	5	3.92	89.00
50	10	3.96	88.43
50	10	3.96	88.43

A model presented by DoE software was fitted with the actual data presented in Equation (4) to describe the effect of the variables examined.

$$\text{Yield} = 199.847 + 0.386D - 3.848C - 0.245D^2 + 0.028C^2 + 0.052DC \qquad (4)$$

The ANOVA results regarding biodiesel yield are summarized in Table 8, where C is the weight fraction of calcium and D is the weight fraction of potassium. The weight fraction of calcium (%) was selected as the effective term with the highest coefficient value and F value. A value of 0.79 for R^2 indicates that some other variables might have interacted on the response, but those variables were not considered in this study.

3. 5. Effect of Calcination Time and Calcination Temperature

The $Ca-K/Al_2O_3$ nanocatalyst for producing biodiesel was prepared. Thereafter, the impact of different weight percents of Ca to K/Al_2O_3 and various operational conditions on the catalytic function of $Ca-K/Al_2O_3$ were examined. The experimental findings at various calcination times and temperatures are indicated in Table 9. The best operational conditions were methanol:oil=9:1 and a catalyst-to-oil mass ratio of 9% at 75°C with mechanical stirring at 500 rpm for 3 h. The optimum catalyst revealed high catalytic performance for producing biodiesel, and the biodiesel yield reached 97%. The physical features, such as viscosity and refractive index, decreased when the biodiesel yield increased; they are suggested as reliable physical properties for calculating biodiesel yield and decreasing the cost of analysis.

A model presented by DoE software was fitted with the actual data presented in Equation (5) to describe the effect of the variables examined.

$$\text{Yield} = -333.362 + 1.210E + 14.554F - 0.001E^2 - 8.421F^2 + 0.059EF \qquad (5)$$

The ANOVA results regarding biodiesel yield are presented in Table 10, where E is calcination temperature and F is calcination time. Table 10 presents statistical characteristics of the chosen significant model terms to

TABLE 8. ANOVA results on the effect of calcium and potassium weight fraction

Source	Coefficient (ß)	F value	P value
Constant	199.847	-	-
D	0.386	0.00	0.952
C	-3.848	5.42	0.059
D^2	-0.245	2.01	0.206
C^2	0.028	6.31	0.046
DC	0.052	1.02	0.352

TABLE 9. The effect of calcination time and calcination temperature on biodiesel yield

Temperature (°C)	Time (h)	Viscosity (cp)	Yield (%)
700	3	4.73	78.99
700	3	4.73	78.99
700	3	4.73	78.99
600	3	4.25	84.74
700	3	4.73	78.99
800	1	16.99	13.01
800	4	5.20	73.77
700	3	4.73	78.99
600	4	3.77	90.95
800	3	3.15	98.3
600	1	4.78	77.52
700	4	3.52	94.41
700	2	2.86	98.01

TABLE 10. ANOVA results on the effect of calcination time and calcination temperature

Source	Coefficient (ß)	F value	P value
Constant	-333.362	-	-
E	1.210	0.53	0.489
F	14.554	0.02	0.898
E^2	-0.001	0.96	0.361
F^2	-8.421	1.34	0.285
EF	0.059	0.31	0.597

indicate the biodiesel yield as a function of the variables examined (that is, calcination time and calcination temperature).

Based on the analysis, second-order calcination time and calcination temperature are significant terms with higher F values and lower P values than other model terms. The determination coefficient (R^2) was computed to be 0.71, which indicates that some other variables might have interacted on the response, but those variables were not considered in this study.

4. CONCLUSIONS

The $Ca-K/Al_2O_3$ heterogeneous nanocatalyst was made ready and used in the transesterification of sunflower oil with methanol or the methanolysis of sunflower oil. The effects of effective parameters on transesterification were investigated. The optimum conditions for the catalytic reaction using the $Ca-K/Al_2O_3$ catalyst were determined

to be 20 wt% Ca and 15 wt% K, a calcination temperature of 800°C for 3 h, a methanol-to-oil ratio of 9:1, a reaction temperature of 75°C, a reaction time of 3 h and a catalyst-to-oil mass ratio of 9%. The optimum catalyst indicated high catalytic function for producing biodiesel, and the biodiesel yield reached 98.3%. The physical features, such as viscosity and refractive index, decreased when biodiesel yield increased; they are suggested as reliable physical properties for calculating biodiesel yield and decreasing the cost of analysis.

5. ACKNOWLEDGEMENT

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Persian Abstract

چکیده

در این مطالعه، شرایط ترانس استریفیکاسیون روغن آفتابگردان با متانول توسط نانوکاتالیست $Ca-K/Al_2O_3$ با استفاده از روش پاسخ سطح بهینه‌سازی شد. متغیرهای مورد آزمایش شامل دمای واکنش (۵۵، ۶۵ و ۷۵ درجه سانتی‌گراد)، زمان واکنش (۱، ۲، ۳، ۴ و ۵ ساعت)، نسبت وزنی کاتالیست به روغن (۳، ۴، ۹ و ۱۲ درصد)، محتوای کلسیم (۲۰، ۳۰، ۵۰، ۶۰ و ۸۰ درصد وزنی)، محتوای پتاسیم (۵، ۱۰، ۱۵ و ۲۰)، نسبت مولی متانول به روغن آفتابگردان (۳:۱، ۶:۱، ۹:۱ و ۱۲:۱)، دمای کلسیناسیون (۶۰۰، ۷۰۰ و ۸۰۰ درجه سانتی‌گراد) و زمان کلسیناسیون (۱، ۲، ۳ و ۴ ساعت) بود. مشخصات کاتالیست با استفاده از نتایج XRD، SEM، FTIR، و TPD مورد آنالیز قرار گرفت. حداکثر راندمان تبدیل استرهای متیل اسید چرب (راندمان تولید بیودیزل) ۹۳ درصد بود که در دمای کلسیناسیون ۸۰۰ درجه سانتی‌گراد برای مدت ۳ ساعت، نسبت متانول به روغن معادل ۹:۱، دمای واکنش ۷۵ درجه سانتی‌گراد، زمان واکنش ۳ ساعت و نسبت جرمی کاتالیست به روغن ۹٪ بدست آمد.