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# Optimization of the activity of KOH/calcium aluminate nanocatalyst for biodiesel production using response surface methodology

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## ABSTRACT

In this study, alumina and calcium aluminate were prepared through microwave combustion method (MCM) and then were modified by potassium hydroxide as solid base catalysts. The catalytic activities were evaluated in the transesterification reaction of canola oil. The characteristic properties of the samples determined by XRD, FTIR, TG, BET surface area, basicity by Hammett indicator, SEM and EDX showed that the alpha phase of alumina and monocalcium aluminate ( $\text{CaAl}_2\text{O}_4$ ) were successfully synthesized by MCM. However, the samples showed less basicity and activity whereas these properties were meaningfully increased by KOH loading. Moreover, the surface area of monocalcium aluminate was increased from 38.9 to 48.1  $\text{m}^2/\text{g}$  by loading of potassium components. To obtain a catalyst with highest activity and basicity, the calcium oxide and potassium group precursor dosages on aluminum oxide were optimized using the response surface methodology (RSM). The optimal parameters obtained were calcium oxide/alumina molar ratio of 1.48:1 and 23 wt.% potassium hydroxide to  $\text{CaO-Al}_2\text{O}_3$ . The yield in the optimal condition was 96.7% (the predicted yield was 98.3%) where the transesterification reaction was performed in conditions of 65 °C, 3.5 wt.% catalyst, 12:1 molar ratio of methanol-to-oil and 4 h reaction time. The catalyst maintained its activity for at least three times.

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## 1. Introduction

Biodiesel is a very popular alternative fuel that is renewable, biodegradable and non-toxic which is commonly produced through transesterification of triglyceride with methanol in the presence of a catalyst. Recently, heterogeneously biodiesel production is widely in consideration to avoid the drawbacks of the homogeneous biodiesel production process and reducing the production costs [1]. In this process, solid base catalysts are extremely utilized due to their higher activity during the transesterification reaction and performing the reaction at a shorter time in comparison to the solid acid catalyst. In this case, many metal oxide catalysts were promoted using the base components such as alkali hydroxide [2–4] and alkaline earth metal oxide [5,6]. The effects of potassium hydroxide and calcium oxide have been extensively evaluated as active phases on the support catalysts due to their high basicity and cheaper resources [7,8]. Many support catalysts have been examined which among them alumina provides more specific surface area, larger distribution of pore sizes and higher stability for active

phases [9]. Alumina promoted by calcium oxide [10–12] and potassium hydroxide [13–16] is meaningfully applied in the biodiesel production. However, according to our knowledge, extensive studies have not yet been performed on the effects of both potassium hydroxide and calcium oxide loading on alumina. Moreover, the researchers reported that the mixture of calcium oxide and alumina could result into many phases of calcium aluminate that are able to affect the basicity and activity due to the presence of different ratios of Ca-to-Al [17–19].

Scientists have applied various catalyst preparation methods that among them, the wet chemical processes such as sol-gel, coprecipitation, impregnation and hydrothermal methods are often utilized. However, these methods require long time, usually more than 2 days for the catalyst preparation which makes these techniques uncommercial, due to consuming expensive raw materials and requiring many processing steps. Nowadays, researchers have proposed other novel methods for producing the catalyst in a short time such as the combustion method. Combustion synthesis is a two-step process: first formation of the precursor and then auto-ignition. This auto-ignition is often termed as the self-propagating high temperature synthesis [20]. Combustion synthesis is particularly an easy, safe and rapid production process wherein the main advantages are savings made in the energy and time. The

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**Table 1**  
Actual and coded values of the variables.

Factor	Units	Low level	High level	Low axial	High axial	Mean
CaO dosage	Mole ratio	0.5 (–1)	1.5 (+1)	0.75 (– $\alpha$ )	1.25 (+ $\alpha$ )*	1 (0)
KOH dosage	Wt.%	0.15 (–1)	0.35 (+1)	0.2 (– $\alpha$ )	0.30 (+ $\alpha$ )	0.25 (0)

The values –1, 0 and 1 in parenthesis are the coded values.

\* Alpha (set at 0.5) is defined as a distance from the center point which can be either inside the range or outside.

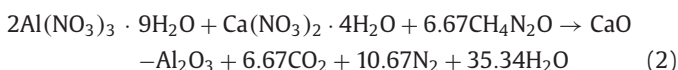
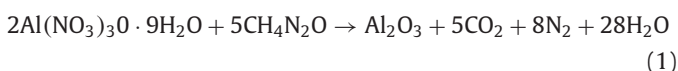
process can be utilized to produce homogeneous, high-purity and crystalline oxide powders [21]. Among various preliminary heat sources that are utilized for starting the combustion reaction, the microwave irradiation has higher ability in preparation of catalyst with larger surface area, pore size, pore volume and higher activity due to the more uniform heating at the molecular level [22].

In this study, the alumina and calcium oxide/alumina catalysts were prepared by MCM and then were impregnated by potassium hydroxide. The catalysts were characterized by XRD, FTIR, BET, FE-SEM and Hammett indicators. The catalytic activity of the samples was assessed for biodiesel production through methanolysis of canola oil. Finally, the concentrations of calcium oxide and potassium hydroxide in the alumina were optimized using the response surface methodology (RSM).

## 2. Experimental

### 2.1. Catalyst preparation

Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and urea with high purities were used as the starting material. The stoichiometric redox mixture of the metal nitrates and urea, to release the maximum energy for the reaction, were mixed with minimum amount of deionized water (30 mL) in a beaker to obtain transparent aqueous solutions. Then, the mixture was continuously stirred and heated to make the viscous gel transparent and then transferred to the domestic microwave oven (Daewoo, Model No. KOC9N2TB, microwave 900 watts). After 2 min, the viscous liquids swelled and auto ignited, with rapid evolution of a large volume of gases to produce voluminous powders. Alumina was produced by the same method without use of calcium nitrate. The reactions between urea and metal nitrate are presented in the following equations:



The KOH promoted catalysts were prepared using the impregnation method. Desirable amount of KOH aqueous solution (based on the weight percentage, see Table 1) was mixed with alumina and CaO-Al<sub>2</sub>O<sub>3</sub> and the mixture was refluxed at 80 °C for 2 h. Afterward the solution turned to the viscous gel, it was dried at 100 °C in an oven overnight in order to remove the water. Finally, the catalyst was calcined in muffle furnace at 700 °C for 5 h.

### 2.2. Catalyst characterization

The X-ray diffraction (XRD) method is used for characterization and identification of the internal structure, bulk phase, and composition in crystalline phases using UNISANTIS/XMP 300, operated at 45 kV and 80 mA by means of Cu K<sub>α</sub> radiation. The XRD patterns were compared to the standards, in order to identify their crystalline phases. The crystallite sizes were calculated using Scherrer equation.

The infrared spectra of the catalyst were recorded using SHI-MADZU 4300 (Japan) spectrophotometer over the range of 4000–400/cm<sup>–1</sup> wavelength and at the room temperature to evaluate the active surface functional groups of synthesized catalysts.

Thermogravimetric (TG) analysis was performed on the support to detect incomplete decomposition of nitrate and urea (as the fuel) during the combustion synthesis and also behavior of the catalyst during calcination using Evolution STA (SETARAM, Ferance) instrument in the range of 50–800 °C at a heating rate of 10 °C/min under the air flow.

The specific surface area and the pore size distribution were determined by the BET and BJH methods using the Belsorp mini II (BelJapan) instrument. Nitrogen gas was used as adsorbate in the analysis. Before starting analysis, the catalysts were heated under vacuum atmosphere at 150 °C for 24 h to eliminate the volatile species adsorbed on the catalyst surface.

The basic strength of the solid bases (H<sub>–</sub>) was determined using the Hammett indicator. The indicators used were as follows: bromothymol blue (H<sub>–</sub> = 7.2), phenolphthalein (H<sub>–</sub> = 9.8), and 2,4-dinitroaniline (H<sub>–</sub> = 15.0). The basicity of the catalysts was calculated by titration of the catalyst-Hammett indicator mixture using benzene carboxylic acid (0.02 mol/l anhydrous ethanol solution) [15,23].

Scanning electron microscopic (SEM) analysis was carried out on the catalyst to study its surface morphology using VP 1450 (LEO – Germany) scanning electron microscope equipped with an energy dispersive spectrometer.

### 2.3. Transesterification reaction

The activity of catalysts was evaluated by transesterification of canola oil in a 100 ml glass reactor equipped with a water-cooled condenser and a magnetic stirrer. The following reaction conditions were set at 65 °C, 3.5 wt.% of catalyst, 700 rpm of the stirring speed, and the methanol/oil molar ratio of 12 and 4 h as is suggested by Zabeti et al. [12]. After separation of the catalyst and glycerol by centrifuging the product mixture at 2500 rpm for 25 min, the biodiesel (upper layer) was purified through heating to cause evaporation of the residual alcohol.

The methyl ester content of biodiesel samples was measured by Teif Gostar Faraz GC-2552 TG gas chromatogram equipped with a Flame Ionization Detector (FID) and capillary column SUPRAWAX-280 (30 m × 0.25 mm × 0.25 μm); the initial temperature was 50 °C, then the temperature was raised with a rate of 8 °C/min to 220 °C and kept for 9 min., again it was increased with a rate of 5 °C/min to the final column temperature of 250 °C and kept for 15 min. The temperature of injector and FID detector was 260 °C and methyl nonadecanoate was used as an internal standard. The conversion was calculated using the following equation:

$$\text{Conversion(\%)} = \frac{[(\text{area of all FAME} \times \text{weight of reference}) / (\text{area of reference} \times \text{weight of biodiesel sample})] \times 100}{\quad} \quad (3)$$

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