K_yMg_1-xZn_1+xO_3 as a heterogeneous catalyst in the transesterification of palm oil to fatty acid methyl esters

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1. Introduction

Fatty acid methyl ester (FAME) is an alternative fuel that can be used as a substitute for conventional petroleum based diesel fuel. FAME is also referred to as biodiesel which include mono-alkyl esters of long chain fatty acids. It is synthesized by replacing glycerol with a short chain alcohol such as methanol or ethanol in a chemical process known as transesterification. Since the rising of crude oil prices in international markets, biodiesel has gain increased acceptability [1]. Various technologies have emerged over the years for biodiesel production and prominent among these is the use of methanol and basic catalysts (mostly KOH) [2].

Today, there are significant demands in energy consumption worldwide; a new and efficient catalyst for FAME production which possesses criteria such as good activity and selectivity, low cost, and environmental friendliness is required. The advantages of FAME includes substantial reduction of unburned hydrocarbons emissions, higher cetane number compared to petro-diesel resulting into higher engine performance [3], higher flash point and superior lubricating properties which increase engine efficiency. It can be used in the engine of automobiles without modifications. It contains no sulphur or aromatic substances associated with fossil fuels. It almost completely eliminates lifecycle carbon dioxide emission. Above all, it is non-toxic and biodegradable; all these properties make biodiesel an environmentally benign fuel [4]. It is indeed an example of environmentally and economically sustainable fuel for the present and future energy needs.

Committed efforts by countries of the world over how to achieve energy independence and remain more environmentally conscious makes utilization of natural resources currently being considered a wise choice. The petroleum based fuel is unhealthy and finite and the current flux of research activities is geared towards moving from this source to domestically produced, cleaner, renewable biodiesel fuel. It is believed that an increase in domestic production of clean-burning and low-cost renewable fuels from a wide array of technologies and feedstock will reduce reliance on imported oil and expand economic opportunities [5].

Generally speaking, the transesterification reaction can be presented by the equation below:

\[ \text{H}_2\text{COOCR} + 3 \text{CH}_3\text{OH} \rightleftharpoons \text{R'COOCH}_3 + 3 \text{CH}_3\text{OH} \]

This is the reaction between a vegetable oil (VO) or animal fat (which are composed of complex mixtures of triglycerides) and a low molecular weight alcohol, such as methanol in the presence of a catalyst [6] either homogeneous or heterogeneous to produce a
complex mixture of fatty acid methyl esters and glycerol, °R° and °R° given in Eq. (1) are hydrocarbon chain from 15 to 21 carbon atoms.

Homogeneous catalyzed processes involving the use of alkali for example, NaOH and KOH [7–9] have been employed to produce biodiesel but they are rather cumbersome. Also due to several disadvantages that accompany the process, biodiesel production becomes expensive and this poses a major barrier to large scale commercialization. Among these include the formation of saponified products because of the presence of free fatty acid in feedstock, interference of water (in raw material) with the reaction, difficulties of separating glycerol and the repeated washing of methyl esters needed for its purification. These have made the development of a heterogeneous catalyst for the transesterification of VOs to produce FAME imperative [10].

Heterogeneous catalysts are much easier to separate from liquid products, they are noncorrosive and environmentally benign [11]. They can be designed to give higher activity, selectivity and longer catalyst lifetime [12]. Briefly, heterogeneous catalysts such as alkali metal (Li, Na, K)-promoted alkaline earth oxides (CaO, BaO, MgO), as well as K2CO3 supported on (Al2O3), have been used for transesterification of Canola oil with molar ratio of alcohol to oil of 11.48:1, catalyst loading of 3.16 wt%, at 60 °C, for 2 h with more than 85% conversion. This requires modification to prevent K leaching [13–16]. Also, transesterification of unrefined or waste oil over lanthanum-promoted zinc oxide (ZnO-La2O3) catalysts, with a 3:1 ratio of zinc to lanthanum, at 170–220 °C, 126 g of oil, 180 g of methanol, and 3 g of catalyst gave over 96% in 3 h [17]. Although raw materials pretreatment was avoided, leaching was not reported [17]. Transesterification of soybean oil using CaO [18] and soybean & poultry fat using nano-crystalline CaO [19] have been reported. Activated CaO on rapeseed oil using 0.10 g catalyst with 3.90 g Methanol, 15 g oil at 60 °C in 3 h, gave 90% [20]. CaO pretreatment was carried out by activation with methanol at 25 °C in 1.5 h before contacting with oil [20]. In a similar work, Nakatani et al. [21] reported transesterification of soybean oil over combusted oyster shells with 25 wt% catalyst, 65–70 °C in 5 h with 73.8% conversion. Mg–Al hydrotalcites was used for transesterification of rape oil at 1.5 wt% catalyst loading, alcohol to oil ratio of 6:1 and 65 °C in 4 h; the yield obtained was 90.5% [22,23]. Silica-supported solid acid catalyst has also been used for the esterification of free fatty acids in sunflower oils (SO) for the production of diesel fuel [24]. Again, basic solid Mg/Zr catalysts have been applied on edible and non-edible oil with Mg/Zr ratio of 2:1 (wt/wt%), when 0.1 g catalyst was mixed with 1 g oil and 2.5 mL methanol at 65 °C for 2 h for transesterification. The results indicated over 90% yield [25]. This gives nearly complete conversion of oils within a short time with large or excess methanol consumption. However, its activity was reduced by the fourth cycle [25]. It is thus clear from the foregoing that despite the huge volume of literature available on the use of heterogeneous catalysts in transesterification, none of the catalysts has completely addressed the problems in the production of biodiesel. Thus, the present work is focused on the transesterification of palm oil with methanol catalyzed by K2MgZnO heterogeneous catalyst and the prediction of the optimum operating conditions to obtain the highest yield of desired product. Effects of various parameters as they affect the process were studied using suitable modelling techniques from response surface methodology and design of experiments. Insights into the structure and chemical surface reactivity of materials are important for heterogeneous catalyst. Based on the characterization of the catalyst using scanning electron micrographs, energy dispersive X-ray, Fourier transform infrared, and X-ray diffraction, the synergetic effect of the catalyst and its activity and the performance were discussed.

2. Materials and methods

2.1. Materials

Commercial edible grade palm oil was purchased from the supermarket at Nilbong Tebal, Malaysia. Analytical reagent grade 99.9% methanol (HPLC) purchased from Merck (Malaysia) was used for the transesterification reactions. Analytical grade of (pro analysis) KOH (≥85%), Mg (NO3)2·6H2O (≥99%), Zn (NO3)2·6H2O (≥98%) and KNO3 (99%), used to synthesize the catalysts were purchased from Sigma–Aldrich Pty Ltd., Malaysia. Methyl heptadecanoate (99.5%) used as internal standard for gas chromatography (GC) analysis was purchased from Sigma–Aldrich (Malaysia) and N-hexane (96%) used as solvent for GC analysis was purchased from Merck (Malaysia). These reagents were used without further purification for catalyst synthesis and the transesterification of palm oil.

2.2. Catalyst preparation

The heterogeneous catalyst, KxMg1−xZn1+xO2 (0.1 ≤ x ≤ 0.9), was synthesized by co-precipitation from nitrate compounds of the metals. Based on 20 g of salt, 50 mL of mixed salt solution containing 1.65576 M of Zn(NO3)2, 0.34424 M of Mg(NO3)2 and 2 M of KNO3 were prepared and mixed in a flask and stirred thoroughly at 600 rpm with a magnetic stirrer. The metals were precipitated using 2 M KOH. The mixture was aged to 80 °C and was stirred continuously for 6 h until the solution is homogenized. The basic strength was determined by the indicator method. The solution was filtered and dried at oven temperature of 85 °C for 12 h. This was followed by thermal treatment at 461 °C for 4 h. The above procedure describes the synthesized catalyst and in particular sample K0.5Mg0.5Zn0.5O2 with Mg: Zn = 1: 4.8. Separate batches of the oxides of MgO and ZnO subjected to the same treatment were precipitated from their nitrates calcined at the same temperature and employed for the transesterification activity immediately.

2.3. Catalyst characterization

The surface area, pore volume and pore size distribution of the developed catalyst were measured by the data from nitrogen adsorption at 77 K adsorption/desorption using ASAP 2020 Micromeritics instrument for the Brunauer–Emmett–Teller (BET) method. Powder X-ray diffraction patterns recorded on a diffractometer (Philips PW 1710) with Cu Kα radiation were used to check the purity and to determine the unit cell parameters of the developed oxide catalyst. The particle microstructures were studied on a Philips XL30S model Scanning Electron Microscope (SEM). The element composition was analysed by using an energy dispersive X-ray detector (EDX) mounted on the microscope. Fourier transform infrared (FT-IR) analysis of the catalyst was carried out to determine the active surface functional groups. The spectra were recorded in the range 4000–400 cm−1.

2.4. Transesterification of palm oil with methanol and quantitative analysis of fatty acid methyl ester content

Palm oil was transesterified with methanol in a 300 mL stainless steel batch reactor (PARR 4842 series reactor) consisting of a four-bladed pitched turbine impeller and a thermocouple. Synthesized catalysts K2MgZnO, MgO and ZnO were tested separately in the methanolysis of palm oil. The reactants were in the liquid phase at atmospheric pressure; mixing commenced immediately after the reactants were charged in before the boiling point of methanol to ensure contact between the oil, alcohol and catalyst. The reactor temperature was controlled with a programmable PID temperature controller.
controller at a heating rate of 3.6 °C/min. The stirrer speed was adjusted to maximum rpm to avoid mass transfer limitations. This was sufficient to keep the system uniform in temperature and suspension. The parameters considered for the reaction were varied according to the experimental design using the response surface methodology (RSM) provided by Design-Expert software version 6.0.6 (Stat-Ease Inc., USA) as presented in Table 1.

At the end of the experiment, the heater and stirrer were switched off and the reactor was cooled to room temperature. After cooling, the catalyst was separated from the product mixture by centrifugation. The product and by product were collected and were allowed to settle. Two phases were formed with methyl esters in the top layer and glycerol in the bottom layer. The top layer product was analyzed by gas chromatography using PerkinElmer Clarus 500 with FID detector, equipped with a fused silica capillary column. Methyl heptadecanoate was used as an internal standard. Injection volume of 1 μL was used and the methyl ester obtained was calculated using the EN14103 application note (the recommended standard for obtaining total FAME content in biodiesel) [26].

2.5. Catalyst stability

The possibility of reusing the catalyst was tested to check its capacity to provide the same catalytic activity. The solid catalyst was recovered after the first run and was washed with methanol to remove any oil that adhered to its surface. The catalyst was filtered and dried for 12 h and without further activation was used in the second and third runs for FAME synthesis by the reaction between methanol and palm oil. Furthermore, the leaching of K from the catalyst was tested by contacting the catalyst with methanol for 2 h at 61 °C. The mixture was filtered to remove the solid catalyst and the filtrate was used in reaction with the triglyceride at the first instance. This procedure was repeated a second and a third times using the solid catalyst recovered from previous batch for contact with methanol in each case. Also, pure methanol and pure oil were mixed together in the same ratio and reacted at the same operating conditions to be exact in the determination of the degree of leaching.

3. Results and discussion

3.1. Characterizations and properties of $K_2Mg_{0.34}Zn_{1.66}O_3$ catalyst

Properties such as BET surface, total pore volume and average pore diameter of solid catalysts are important during
The external surface area of the catalyst is known to favour reactivity and is directly proportional to it. Table 2 shows the characteristics of the catalyst used for the transesterification. By use of SEM, the catalyst microstructure was examined. Fig. 1a is the SEM image of a typical catalyst K$_2$Mg$_{0.34}$Zn$_{1.66}$O$_3$ that was synthesized for the purpose of transesterification of palm oil in this work. The image shows that the surface comprises a large number of agglomerates of catalyst particles. It also revealed the porous nature of the catalyst. This structural pattern is considered to be one of the reasons for its high activity. Similar images were obtained for MgO and ZnO, as shown in Fig. 1b and c respectively.

The composition of the catalyst was verified by using an EDX mounted on the microscope and the elemental analysis revealed that the sample contained 74.01 wt% Zn, 7.18 wt% Mg, 1.08 wt% K and 17.73 wt% O. This was in good agreement with the XRD diffraction patterns which showed basically ZnO and MgO peaks as 31.73 and 17.73 wt% O. This was in good agreement with the XRD that the sample contained 74.01 wt% Zn, 7.18 wt% Mg, 1.08 wt% K and 17.73 wt% O.

Table 3
Factors and corresponding levels for the response surface design (real and coded independent variables).

<table>
<thead>
<tr>
<th>Factor</th>
<th>Factor code</th>
<th>Unit</th>
<th>Low (-1)</th>
<th>Central (0)</th>
<th>High (+1)</th>
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<tr>
<td>Temperature</td>
<td>C</td>
<td>°C</td>
<td>150</td>
<td>175</td>
<td>200</td>
</tr>
<tr>
<td>Reaction time</td>
<td>A</td>
<td>h</td>
<td>0.5</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>Methanol/oil ratio</td>
<td>B</td>
<td>-</td>
<td>3:1</td>
<td>12:1</td>
<td>20:1</td>
</tr>
<tr>
<td>Catalyst loading</td>
<td>D</td>
<td>wt% of oil</td>
<td>1.4</td>
<td>2.5</td>
<td>5.0</td>
</tr>
</tbody>
</table>

where they significantly alter surface reactivity and are responsible for the high activity. This fact is supported by the works of Berger et al. [27] and Ramu et al. [28] where the applications of heterogeneous catalysts appear to give higher reactivity as a result of the structural stability.

Similarly, the FT-IR spectra analysis of the catalyst is shown in Fig. 3, which represents the MgO and ZnO mixed oxides and the combination of the two oxides with K. In the spectrum of K$_2$MgZnO, the appearance of a peak at 3218–3854 cm$^{-1}$ indicates the presence of O–H stretching and water molecules. The hydroxyl group is dominant and does not exist in isolation. The significant band broadening and the lowering of the absorption frequency indicate the presence of both inter and intra molecular hydroxyl functional groups. This tends to be a function of the degree and strength of the hydrogen bonding which here is a characteristic of hydroxides with a large shift, thus lower frequency is observed. The extension of this broad band in the range of 2376–2395 cm$^{-1}$ indicates the presence of interlayer water molecules bonded to the hydroxyl ions. The catalyst exhibits a peak centered at 1385 cm$^{-1}$ with a broad band arising from the strong Mg–O–Zn network; as the broad band increases, it suggests either a change in the metal oxide complex symmetry in the catalyst, or the evolution of an asymmetric Mg–O–Zn mode. This is in agreement with the work of Rao et al. [29]. The bands at 1053–1084 cm$^{-1}$ represent M–O vibration and those at 826–936 cm$^{-1}$ give the M–O–H bending.

3.2. Process optimization and statistical analysis

The experimental results of the four main parameters studied (i.e. time, methanol/oil molar ratio, temperature and catalyst loading) were subjected to response analysis to evaluate the relationship between them. The matrix corresponding to the central composite design in terms of real and coded independent variables is presented in Table 3. The high and the low values corresponding to each factor were carefully selected based on preliminary experimental results and after reviewing the related literature [30,31].

The experimental results were fitted to both linear and 2FI models which resulted in Eqs. (2) and (3) given below in terms of actual factors as:

\[
\text{FAME content} = +0.95969 + 2.14339 \times A + 0.25646 \times B + 0.34393 \times C + 1.87999 \times D
\]

where \(A = \text{time}, \ B = \text{methanol/oil molar ratio}, \ C = \text{temperature}, \) and \(D = \text{catalyst loading};\) and for the 2FI model as:

\[
\text{FAME content} = -154.30299 + 28.53035 \times A + 4.04723 \times B + 0.86434 \times C + 30.02891 \times D
\]

\[
-0.18645 \times A \times B - 0.084110 \times A \times C - 2.97578 \times A \times D - 5.13937 \times 10^{-3} \times B \times C - 0.71409 \times B \times D - 0.058679 \times C \times D
\]

The confidence interval for both models which is statistically significant was given as 95% confidence but could not adequately...
represent the system. Hence, a more complex design was required to fit the data to the full second-order model in four variables. This argument is substantiated by the work of Vicente et al. [32] where a comparison between the linear and quadratic models gave better results for the quadratic model on the 3D surface plot. Thus, the data fitted well into the second-order polynomial model equation expressed by Eq. (4)

\[
\text{FAME content} = -517.83435 + 32.89119 \times A + 6.28414 \times B \\
+ 4.69427 \times C + 38.47230 \times D - 0.70110 \times A^2 \\
- 0.095074 \times B^2 - 0.010927 \times C^2 \\
- 1.27700 \times D^2 - 0.18429 \times A \times B \\
- 0.083373 \times A \times C - 2.96265 \times A \times D \\
- 5.37759 \times 10^{-3} \times B \times C - 0.71833 \times B \times D \\
- 0.060122 \times C \times D
\]

The summary of the analysis of variance (ANOVA) which is important to determine the adequacy and significance of the quadratic model was obtained and is presented in Table 4. The model F-value of 8.79 implied that the model was significant and there was only a 0.01% chance that a model F-value as large as this would occur due to noise. P-value less than 0.0500 indicated the significant model terms. A low value of coefficient of the variation (CV, 5.88%) indicated a high degree of precision and a good deal of reliability of the experimental values. The regression analysis of the experimental design demonstrated that the linear model terms (A and C) and the interactive model terms (AD, BD) are significant (P < 0.0001). The second-order polynomial model obtained for the result was utilized for the dependent response (FAME content) in order to determine the specified optimum conditions. The second-order was assumed based on the design programme that was used for the analysis of the result. The central composite design of the software was able to function as an optimal design for the desired response of the system based on the model obtained and the input criteria. The optimization of FAME was carried out based on all transesterification variables, which were in the range of experimental runs as indicated in Table 5. In this particular case, the software predicted that optimized conditions for the yield of FAME were obtained when the temperature, methanol to oil molar ratio, amount of catalyst and reaction time, took values 188°C, 19 molar ratio, 1.7 wt% of catalyst, and 4 h respectively. The predicted value of FAME at the optimum conditions was given as 92%. However, the experimental yield gave 80% under the same optimum conditions. Thus, it would be reported as observed in this work that the experimental value obtained was in good agreement with the value calculated from the model. Three-dimensional response surface plots were generated with two variables kept at the central level (0), and varying the others within the experimental range as shown in Figs. 4 and 5.

3.3. Effects of different parameters on the transesterification of palm oil

Methanolyis of palm oil requires three moles of methanol for each mole of oil according to the stoichiometric Eq. (1). Since the transesterification of triglycerides is a reversible reaction, excess methanol shifts the equilibrium towards the direction of ester formation. The effect of reaction time and catalyst loading on FAME

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**Table 4**

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>DF</th>
<th>Mean square</th>
<th>F-value</th>
<th>Prob &gt; F</th>
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<td>209.27</td>
<td>10.20</td>
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<tr>
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<td>1</td>
<td>28.15</td>
<td>1.37</td>
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</tr>
<tr>
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</tr>
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<td>64.98</td>
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<tr>
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<tr>
<td>BD</td>
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<td>20</td>
<td>20.52</td>
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<tr>
<td>Lack of fit</td>
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<td>18</td>
<td>21.45</td>
<td>1.76</td>
<td>0.4231</td>
</tr>
<tr>
<td>Pure error</td>
<td>24.33</td>
<td>2</td>
<td>12.16</td>
<td></td>
<td></td>
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<tr>
<td>Cor. total</td>
<td>1492.76</td>
<td>26</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The preset goal with constraints for all parameters and response for optimization conditions.

### Table 5

<table>
<thead>
<tr>
<th>Constraints</th>
<th>Lower limit</th>
<th>Upper limit</th>
</tr>
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<tbody>
<tr>
<td>Name</td>
<td>Unit</td>
<td>Goal</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>Is in range</td>
</tr>
<tr>
<td>Reaction time</td>
<td>h</td>
<td>Is in range</td>
</tr>
<tr>
<td>Methanol/oil ratio</td>
<td></td>
<td>Is in range</td>
</tr>
<tr>
<td>Catalyst loading</td>
<td>wt% of oil</td>
<td>Is in range</td>
</tr>
<tr>
<td>FAME content</td>
<td>%</td>
<td>Maximize</td>
</tr>
</tbody>
</table>
that at a fixed catalyst loading (2.5 wt%), the FAME content increased with temperature up to a critical value, beyond which a decrease in yield was observed. Briefly, the mechanism of the process involves the interaction of the catalyst with the protons generated from the alcohol solvent and the mixed oxides catalyst with the alkyl group of fatty acid and of triglycerides to form a nucleophile followed by proton transfer and re-arrangement. The observed decrease may be due to mass transfer limitations likely related to blockage of catalyst active sites by these compounds. Other authors [33,34] have also reported similar results. The interactions between these catalyst loading and methanol/oil molar ratio presented in Fig. 5b were observed to be very significant and this was confirmed by the work of Srilatha et al. [35]. The effect of methanol to oil ratio on the yield of FAME investigated revealed that there was a proportionate increase in yield as the ratio was increased. However, above the ratio of 16:1 the conversion decreased. Thus, it is evident that to obtain higher conversion, excess of methanol was effective to a certain extent. A comparison of the activities of separate oxides of MgO and ZnO clearly showed that the synergistic effect of the two oxides gave higher activity. Table 6 illustrates the independent activities of MgO and ZnO. The synergistic effect could be due to the modification of the electronic properties of the synthesized KMgZnO catalyst through the interactions of the metal anions. Due to low basicity of Zn, the thermally treated Zn precipitate gave a negligible amount of methyl esters. On the other hand, the mixed oxides of Mg and Zn prepared via co-precipitation enhanced the methyl ester formation. Nakajima et al. [36] developed an active carbon-based solid acid catalyst that is environmentally benign to produce useful chemicals and conversion of vegetable oil to biodiesel in a one-step process. They obtained a conversion between 80% and 90% of ethyl oleate and ethyl stearate. Although, the preparation method employed in their study of the solid catalyst is hazardous, its activity is quite good. The KMgZnO heterogeneous catalyst synthesized in this work has an advantage of simplicity, affordability, and ease of handling in its method of preparation. In a similar work, Xu et al. [37] developed a mesoporous polyoxometalate-tantalum pentoxide composite catalyst, $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{Ta}_2\text{O}_5$ with $\text{H}_2\text{PW}_{12}\text{O}_{40}$ loading of 3.6–20.1% by a one-step sol–gel hydrothermal route in the presence of a triblock copolymer surfactant. The catalytic performance of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was evaluated in the esterification of lauric acid and myristic acid; and on transesterification of tripalmitin under mild conditions. High reactivity and selectivity was reported and when compared with the present work; co-precipitation method was used to synthesize the catalyst for transesterification of palm oil. It should be noted however, that preparation method, calcination temperature and time cum catalyst composition have great effect on catalytic activity and are often the variables of catalyst preparation that have effects on performance. Furuta et al. [38] developed a solid superacid catalyst and employed the use of flow reactor at very high methanol to oil ratio of 40 for transesterification of soybean oil. A

![Fig. 5.](image)

(a) Three-dimensional response surface plot of FAME content showing effect of methanol to oil molar ratio and time (temperature = 175 °C, catalyst loading = 2.5 wt%). (b) Three-dimensional response surface plot of FAME content showing effect of catalyst loading and methanol to oil molar ratio (temperature = 175 °C, time = 3 h).

<table>
<thead>
<tr>
<th>Catalyst Synthesis method</th>
<th>Methyl ester content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO*</td>
<td>Precipitation</td>
</tr>
<tr>
<td>ZnO*</td>
<td>Precipitation</td>
</tr>
<tr>
<td>$\text{KMg}<em>{0.34}\text{Zn}</em>{1.66}\text{O}_3$</td>
<td>Co-precipitation</td>
</tr>
<tr>
<td>$\text{K}_2\text{MgZnO}_3$</td>
<td>Co-precipitation</td>
</tr>
</tbody>
</table>

* Transesterification conditions: catalyst amount, 1.4 wt%; methanol/oil ratio, 6:1; temperature, 150 °C; time, 6 h; atmospheric pressure.

* Transesterification conditions: catalyst amount, 2.3 wt%; methanol/oil ratio, 16:1; temperature, 188 °C; time, 5 h; atmospheric pressure.
conversion of over 90% was obtained at extremely high temperatures (250–300 °C) and 20 h on stream. High activity of the catalyst was reported at these conditions but the experimental conditions of the present work seems to be more favourable economically when compared with the work of Furuta et al. considering the amount of energy utilization at 20 h reaction time and at such a high temperature (250–300 °C) the process may no longer be economical. Ebiura et al. [39] in their work carried out selective transesterification of triolein with methanol to methyl oleate and glycerol using alumina loaded with alkali metal salt as a solid–base catalyst. The results of their investigations revealed that K2CO3 supported on Al2O3 gave 93% and 87% yields in 1 h of methyl oleate and glycerol at 333 K reaction temperature respectively. The 87% of FAME yield obtained in the present work showed a high activity of the catalyst at the operating conditions which compares favourably with their findings, since palm oil was used as a basestock material.

3.4. Catalyst stability

Reusability is one of the important tests required to determine the economical application of K>MgZnO as heterogeneous catalyst for biodiesel synthesis. Table 7 shows the results obtained for the reusability and the leaching tests for the synthesized catalyst after successive runs. As may be observed from the table, there was a downward trend in the performance of the catalyst regarding its reusability. At its first use, 71% of FAME yield was obtained, while the second and third use resulted in 47% and 19% FAME yield respectively. The catalyst was recovered after each run by washing with methanol, it was filtered and dried at 85 °C for 3 h and was placed in contact with fresh portions of methanol and palm oil. The decline in activity could be due to either deactivation of the active sites of the catalyst as a result of poisoning by some molecules present in the reaction mixture and may be regenerated to reverse deactivation or due to leaching of the active phase to the alcoholic phase in which the catalyst would have a smaller number of active sites in the successive runs; in this case reactivation is not possible [40]. EDX analysis of the catalyst after first contact also revealed the presence of carbon (C = 4.39 wt%), Mg = 9.42 wt%, and K = 0.45 wt%) which could have inhibited the catalyst active pores. However, the results of the leaching test for three successive runs showed a decline in FAME content for the first, second and third contacts with a value of 13%, 6% and 3% respectively. In each case, the catalyst was placed in contact with methanol at 61 °C for 2 h. The mixture was filtered and the clear methanol solution was used with the vegetable oil. It will be observed from Table 7 that 34% of the catalyst activity was lost between the first and second runs. Of this value, 4% was found in the filtrate, an indication that 12% of the lost component was leached. Thus, the observed leaching in this work is in the range of 4% to 13% when the leached and the lost components are taken into consideration. In the case of the second and third leaching tests, the observed pattern for this could be due to a number of reasons. First, there could be a lowering in the number of catalytic sites probably due to an interaction of the solid catalyst with methanol at higher temperatures, in which case the complex formed between the methanol and the catalyst became less effective in the transesterification than just pure methanol and vegetable oil subjected to the same reaction temperature and time. As noted in Section 2.5, a mixture of pure methanol (i.e. without contact with the catalyst) and vegetable oil was subjected to the same reaction conditions, and the result as shown in Table 7 revealed that there was a 9% FAME yield. Second, the decline could be due to leaching of soluble components during the treatment with methanol, and third the trend could be explained when losses during the manipulation of the catalyst are considered. Although the leaching in this work is considerable, in spite of it, the selectivity of the catalyst at high temperature is valuable and future efforts will be directed towards overcoming the problem.

4. Conclusion

It can be concluded that fatty acid methyl esters have been produced from the transesterification of palm oil using active heterogeneous K>Mg1–xZnx1–yO3 mixed oxides catalyst that separates easily from the product mixtures. Synergetic interaction between zinc, magnesium and potassium species was observed from the high activity of the FAME produced. Further investigations into the activities of independent component of the metal species gave lower yield when subjected to the transesterification process under the same catalyst preparation and activity with the optimal conditions. Thus, this research work revealed that the performance of heterogeneous catalyst of the type K>Mg1–xZnx1–yO3, gave an optimal value of 87% FAME at 188 °C, under atmospheric pressure in 5 h. The active mixed oxide of K>MgZnO for the transesterification can be successfully prepared by the co-precipitation of the corresponding mixed metal nitrate solution in the presence of KOH as precipitating agent. The combination of FT-IR, SEM, and XRD results indicated the presence of surface amounts of acid and base sites which enhanced the catalyst performance in the transesterification reaction. In addition, this catalyst is cheap because of the availability of raw materials used and the preparation procedure adopted in the study. Above all, product separation and purification process is simple because the catalyst separates easily from the ester mixture after production and it is reusable though with some amount of leaching which after purification could make biodiesel more available and at a reduced cost of production.

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References


Table 7

<table>
<thead>
<tr>
<th>Methanol + vegetable oil (% FAME content)</th>
<th>Reusability test (% FAME content)</th>
<th>Leaching test (% FAME content)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No catalyst (blank)</td>
<td>9</td>
<td>–</td>
</tr>
<tr>
<td>1st run</td>
<td>71</td>
<td>13</td>
</tr>
<tr>
<td>2nd run</td>
<td>47</td>
<td>6</td>
</tr>
<tr>
<td>3rd run</td>
<td>19</td>
<td>3</td>
</tr>
</tbody>
</table>

* Transesterification conditions: catalyst amount, 1.4wt% of oil (1.2 g); methanol/oil ratio, 6:1; temperature, 150 °C; time, 6 h; atmospheric pressure.