



Montmorillonite K10-supported CaO–MgO catalyst for biodiesel production from *Jatropha curcas*: Taguchi (L9) optimization

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Abstract

Biodiesel production can be made more sustainable by utilizing non-edible feedstock and heterogeneous catalysts, thus ensuring clean and affordable energy in conformity with the sustainable development goal (SDG 7). Herein, a reusable mixed metal (Ca–Mg) oxide-laden montmorillonite K10 (CaO–MgO@MK10) was developed by coprecipitation-impregnation method at different $\text{Ca}^{2+}/\text{Mg}^{2+}$ molar ratios followed by calcination at 700 °C for 4 h to ensure the Ca–Mg oxide deposition on MK10 surface for biodiesel synthesis via methanolysis of *Jatropha curcas* oil (JCO). The evaluation of the catalysts' physicochemical properties and activity using various analytical methods and catalytic tests showed that the CaO–MgO@MK10 composite prepared at a 1.5:1 $\text{Ca}^{2+}/\text{Mg}^{2+}$ molar ratio (CaO–MgO@MK10-1.5:1) exhibited best catalytic activity for transesterification of JCO, ascribing to high basicity ($15.0 < \text{H}_+ < 18.4$), large surface area ($93.0 \text{ m}^2 \text{ g}^{-1}$), mesoporous structure and well dispersed Ca–Mg oxides on MK10 support. Optimization of methanolysis of JCO with a CaO–MgO@MK10-1.5:1 catalyst using Taguchi method determined optimum conditions ($\text{CH}_3\text{OH}/\text{JCO}$ ratio of 12:1, methanolysis temperature of 60 °C, catalyst concentration of 3 wt% and reaction duration of 3 h), under which the maximum biodiesel yield of $97.2 \pm 0.17\%$ was achieved. The FAME content in the optimal biodiesel sample was 97.85 wt%, according to GC-MS analysis, exceeding the EN 14,214 biodiesel standard of 96.5 wt%. Moreover, CaO–MgO@MK10-1.5:1 was proven to be stable after being reused for 7 times with a minimal leaching of <15%, indicating its promising industrial application potential.

Keywords CaO–MgO@MK10 · Transesterification · Biodiesel · Catalyst characterization · Taguchi design

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Introduction

The level of utilization of fossil fuels increases daily due to industrialization and globalization, depleting the non-renewable fuel reserves and degrading the environment [1]. Sourcing alternative fuel, such as biodiesel, is required to address the aforementioned twin crises and enhance energy security for socio-economic development. Biodiesel is a renewable liquid fuel derived from triglyceride-containing feedstocks (oils from animal or plant), typically by the alcoholysis process, which uses acids, bases, or enzymes as catalysts [2, 3]. Catalysts do exist in either heterogeneous or homogeneous phase. Homogeneously catalyzed transesterification demands the use of catalyst and reactants from the same phase, thus making catalyst recovery difficult and promoting wastewater formation [4]. In contrast, using a solid (heterogeneous) catalyst in the transesterification process encourages catalyst reuse and discourages waste generation, lowering total production costs and ensuring sustainability [5, 6].

Recent research focuses on development of active solid catalysts that are both deactivation resistant and recyclable, and it is well documented that oxides of alkaline earth metals, like CaO, MgO, BaO etc., are commonly used heterogeneous catalysts for biodiesel synthesis because they are non-toxic, not soluble in simple alcohol, basic in nature, less harmful to the environment and can be sourced from waste materials [7, 8]. Degfie et al. [9] catalyzed used frying oil (UFO) biodiesel synthesis by nano CaO at 50 °C for 1.5 h with 8:1 CH₃OH/UFO ratio and 1 wt% CaO concentration, resulting in 96% biodiesel yield. In the work reported by Ashok and his co-authors, nano MgO was used as catalyst for UFO biodiesel production via methanolysis at 65 °C for 1 h with 24:1 CH₃OH/UFO molar ratio and 2 wt% MgO concentration, which offered biodiesel yield of 93.3% [10]. Furthermore, methanolysis of *Reutealis trisperma* oil over Ca–Zn mixed oxides catalysts offered 98% biodiesel yield under optimized condition of CH₃OH/oil molar ratio of 30:1, reaction time of 2 h and Ca/Zn ratio of 1:1 [11]. However, none of these catalysts were reused, most likely due to leaching of active components, which can be curbed by promoting metal-support interactions, encapsulating the active ingredient and modifying the catalyst support [1, 12, 13].

The utilization of clay minerals as catalytic support for reaction process is an exciting aspect of green chemistry. MK10, a type of clay material that could be locally sourced, has been used as a support for catalyst formulation owing to its favourable characteristics like high surface area, non-toxicity, inexpensiveness, good selectivity and chemical stability [2, 4]. Unmodified MK10 has been proven to be less effective and produce less active solid catalysts, indicating that catalysts of only low activity could be produced

from this relatively mild acid-activated clay [4, 14]. Thus, modification of clay material is pertinent to improving its acidic or basic attributes and circumvents the shortcoming of clay minerals vis-à-vis relatively low activity. MK10 supported iron showed excellent performance in the WCO transesterification with CH₃OH being able to offer 95.3% biodiesel yield as compared to unmodified MK10 catalyst that yielded 38.4% biodiesel [15]. Thus, MK10 was considered as a preferred catalyst support for heterogeneously catalyzed methanolysis process. Meanwhile, CaO–MgO, a mixed alkaline earth metal oxide, is regarded as a promising catalyst that may exhibit excellent catalytic performance and stability due to the strong interaction between Ca²⁺ and Mg²⁺ caused by co-precipitation, particularly at the appropriate Ca²⁺/Mg²⁺ molar ratio, thereby improving the basic properties of the clay support and forming a bifunctional catalytic site [11, 16]. On this premise, it is fair to believe that the MK10-supported CaO–MgO catalyst could be an effective solid base catalyst for biodiesel production via the transesterification process. As far as we know, this type of study has yet to be reported.

It has been proven that transesterification process conditions significantly influence a heterogeneous catalyst's performance, thus optimizing the conditions are crucial for achieving desired biodiesel yield [11, 17]. In assessing the holistic effects of the transesterification process conditions on clay supported mixed metal oxides performance, the application of experimental design methodology is particularly necessary. Taguchi design method has been found to be useful to systematically study the influences of multiple variables on a response parameter, while reducing the experimental runs [2, 18]. In this study, however, it is aimed to optimize for the first time the montmorillonite K10 (MK10) supported CaO–MgO-catalyzed biodiesel synthesis from *Jatropha curcas* oil (JCO) using Taguchi approach. The utilization of second-generation biodiesel feedstock, like JCO, to synthesize biodiesel will minimize the production cost and erase the fear of food versus energy crisis. *Jatropha curcas* seed contains almost 35% oil which comprises of various fatty acids with linoleic and oleic acids (unsaturated components) practically more than other components, thus rendering the non-edible oil suitable for biodiesel synthesis [19, 20]. Thus, the present study investigated the biodiesel synthesis via methanolysis of JCO over mixed alkaline earth metals (Ca–Mg) enriched MK10 catalyst. The transesterification process parameters (temperature, catalyst concentration, CH₃OH/JCO ratio and time) influences on the yield of biodiesel were evaluated by using Taguchi optimization approach. Moreover, the possible recycling of the catalyst was evaluated to ascertain its stability in biodiesel production. As the catalytic potential of CaO–MgO@MK10 composite is investigated further, it is expected that this

discovery will open the way for a sustainable and efficient method of producing biodiesel, given that both methanol and *Jatropha curcas* are inexpensive.

Methodology

Materials

JCO was collected from a separation process laboratory, ABUAD, Ado-Ekiti, Nigeria and immediately analyzed to determine its acid value, moisture content, kinematic viscosity and relative density which were $15.4 \text{ mg KOH g}^{-1}$, 0.06%, $31.5 \text{ mm}^2 \text{ s}^{-1}$ and 0.921, respectively. Analytical-grade reagents used herein, such as calcium nitrate dihydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$), magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Na_2CO_3 , MK10, n-hexane and methanol, were bought from a local supplier in Ado-Ekiti, Nigeria.

Catalysts formulation

Various solid catalysts (CaO@MK10 , MgO@MK10 and CaO-MgO@MK10) were prepared using co-precipitation-impregnation technique. To produce CaO@MK10 and MgO@MK10 catalysts, 2 g each of $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were charged into separate beakers containing deionized water (50 mL), and Na_2CO_3 solution was added drop wise to the mixture while stirring continuously at 250 rpm and 40°C until pH of the mixtures attained 10. For the preparation of CaO-MgO@MK10 composites, certain amounts of $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (0.018 mol and 0.04 mol) and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.027 mol) corresponding to $\text{Ca}^{2+}/\text{Mg}^{2+}$ molar ratios (1:1.5 and 1.5:1) were dispersed in deionized water (50 mL). Then, aqueous Na_2CO_3 solution added drop by drop to the mixture while stirring continuously at 40°C until the pH of the mixtures reached 10. Thereafter, the required quantity of MK10 was added to the prepared mixtures, agitated for 5 h and aged for 15 h for proper impregnation. The slurries were thereafter filtered to obtain residues that were dried in an oven at 110°C for 10 h. Finally, the dried materials were calcined at 700°C for 4 h in a muffle furnace. The resulting MK10 supported Ca-Mg mixed oxides catalysts were labeled as $\text{CaO-MgO@MK10-}x:y$, where $x:y$ indicates $\text{Ca}^{2+}:\text{Mg}^{2+}$ molar ratio.

Catalyst properties evaluation

The properties of the as-synthesized solid catalysts were determined by different characterization devices, including Quanta 200 F-FEI scanning electron microscopy-energy dispersive X-ray analyzer to evaluate the surface morphology and elemental compositions of the samples, Thermofisher

Scientific FTIR spectrophotometer to determine the surface functional groups, X-ray diffractometer (AXS-Bruker) with Cu- α ($\lambda = 1.54 \text{ \AA}$) to characterize crystal structure and chemical phase composition and ASAP2420 Micromeritics porosity analyzer to measure surface area, pore size and pore volume under N_2 sorption at -77 K . Furthermore, basic strength of the solid samples was evaluated by using Hammett indicator approach reported by Alsharifi and Znad [5] with little modification, which required mixing of catalyst sample (30 mg) with 10 mL solution of Hammett indicator and allowing the mixture for a while to equilibrate. The catalyst colour change was then noted. The indicators used for this investigation were neutral red ($H_- = 6.8$), bromothymol blue ($H_- = 7.2$), phenolphthalein ($H_- = 9.3$), alizarin yellow ($H_- = 11.0$), 2, 4-dinitroaniline ($H_- = 15.0$) and 4-nitroaniline (18.4).

Catalytic activity studies

Herein, two-step transesterification reaction process was adopted due to high FFA content in the feedstock, and to reduce the acid content to acceptable level of $<3.0 \text{ wt\%}$ [1, 20], 100 mL of JCO underwent esterification reaction with 50 mL of CH_3OH using H_2SO_4 (2 wt%) as a catalyst at 60°C for 1.5 h, reducing the acid content to $1.97 \text{ mg KOH g}^{-1}$ from $15.4 \text{ mg KOH g}^{-1}$. Thereafter, the esterified JCO was converted to biodiesel via transesterification process which took place in a 100 mL 2-neck round bottom flask equipped with condenser and thermometer. The flask and its content were immersed in silicon oil to regulate the reaction temperature. Firstly, needed amount of the composite catalyst was mixed with CH_3OH to form metal methoxide at preset temperature, then certain amount of esterified oil was added, and continuous mixing thereafter began immediately to facilitate appropriate contact between the catalyst and reactants. The reaction product was thereafter centrifuged at 7000 rpm for 5 min to recover the spent catalyst before being left to separate further. The excess CH_3OH was separated using a rotary evaporator, the produced biodiesel was weighed and its yield calculated using Eq. 1.

$$Y = \frac{M_{JCO-B}}{M_{JCO}} \times 100\% \quad (1)$$

where Y , M_{JCO-B} and M_{JCO} are biodiesel yield (%), mass of produced biodiesel and mass of pretreated oil used, respectively.

Experimental design via Taguchi approach

Taguchi method is one of the statistical experimental design techniques that specialize in minimizing variability and

Table 1 Taguchi L_9 (3^4) orthogonal array for biodiesel production process conditions

Factor	Levels		
	Low	Middle	High
Temperature, T_T (°C)	50	60	70
time, t_T (h)	3	4	5
CH ₃ OH/JCO molar ratio, M	8:1	10:1	12:1
Catalyst concentration, C (wt%)	1	2	3

Table 2 Textural and basic properties of the catalytic materials and biodiesel yields

Sample	S_{BET}^a (m ² g ⁻¹)	PV^b (cm ³ g ⁻¹)	APD^c (nm)	Basic strength (H ₊) ^d	Bio- diesel yield ^e (%)
MK10	217.4	0.373	6.51	6.8 < H ₊ < 7.2	18.2
CaO@MK10	29.8	0.113	17.51	9.8 < H ₊ < 18.4	84.5
MgO@MK10	4.32	0.018	21.62	9.8 < H ₊ < 15.0	77.1
CaO–MgO@ MK10-1.5:1	93.0	0.197	8.34	15.0 < H ₊ < 18.4	95.2
CaO–MgO@ MK10-1:1.5	69.4	0.176	9.38	9.8 < H ₊ < 15.0	90.6

enhancing quality through the utilization of orthogonal arrays. It prioritizes modeling and analysis of problems in which a process output of interest is impacted by many variables [21]. In this work, Taguchi orthogonal array design was applied to investigate the influence of methanolysis conditions on yield of biodiesel, reducing the number of experiments required, reagents consumption and experiment time. The independent variables considered were temperature, catalyst concentration, CH₃OH/JCO molar ratio, while the dependent parameter was yield of biodiesel. Each of the controllable variables at three levels (low, middle and high), as presented in Table 1, were introduced to Minitab 18 statistical software, which proposed nine sets of experimental conditions (see Table 2).

In this experimental design method, the deviation of experimental data to the desired value is estimated, and the deviation is then transformed into signal/noise ratio (S/N ratio) which is the logarithmic function of the expected outcome that is used for the objective of the optimization of the process output [11]. The S/N ratio is often expressed in three different forms, namely nominal is the best, larger the better and smaller the better [21]. In this study, however, the objective of the process optimization is to maximize the biodiesel yield, thus the S/N ratio corresponded to the “larger the better” goal illustrated by Eq. 2 was applied.

$$S/N = -10 \log \left[\frac{1}{n} \sum_{i=1}^n \frac{1}{y_i^2} \right] \quad (2)$$

where n and y_i are number of repetitions under identical conditions and the measured response, respectively.

Moreover, a mathematical relation that described the relationship between the dependent variable (biodiesel yield) and the four transesterification process parameters is given in Eq. (3), as suggested by the Minitab 18 statistical software.

$$Y = b_o + b_{T_T} T_T + b_{t_T} t_T + b_M M + b_C C \quad (3)$$

where Y is the predicted yield of biodiesel (response) and b_o - constant coefficient. b_{T_T} , b_{t_T} , b_M , and b_C are linear coefficients of transesterification temperature (T_T), transesterification time (t_T), CH₃OH/JCO molar ratio (M) and catalyst concentration (C), respectively.

Catalyst stability evaluation

One of the benefits of heterogeneous catalysis over homogeneous catalysis is the catalyst reusability, which lowers total production costs and prevents wastewater generation. Following the reaction, the product stream was centrifuged to reclaim spent catalyst, which was immediately rinsed with n-hexane (50 mL) to remove adhered organic compounds before being oven-dried at 60 °C overnight. The dried sample was then recalcined at 550 °C for 70 min for reactivation and subsequently reused for methanolysis process under optimum reaction conditions. The quantity of JCO needed for each reaction cycle was estimated using Eq. 4, which illustrated the relationship between the amount of recovered catalyst and the amount of JCO needed for subsequent reaction cycle. Meanwhile, the CH₃OH volume used for each cycle was estimated based on the optimal molar ratio of alcohol to JCO.

$$\frac{W_{OI}}{W_{CI}} = \frac{W_{OF}}{W_{CF}} \quad (4)$$

where W_{OI} , W_{OF} , W_{CI} and W_{CF} are initial weight of oil used, final weight of oil used (g), W_{CI} initial weight of catalyst recovered (g) and final weight of catalyst recovered (g), respectively.

Optimal biodiesel characteristics evaluation

Optimal biodiesel sample was evaluated as per fuel and physicochemical characteristics by using various ASTM testing techniques to determine specific gravity, kinematic viscosity, cloud and pour point and flash point. Moreover, the FAME content in the biodiesel sample produced under optimum conditions was measured with the aid of GC-MS (Varian 3800/4000) and a VF-5MS capillary column (30 m, 0.25 mm internal diameter, 0.25 mm thickness) by diluting 20 μ L of biodiesel sample with 200 μ L of methyl

heptadecanoate which was utilized as an internal standard. Subsequently, 1.00 μ L of the mixture was taken and introduced into the GC-MS device. The column was operated in a temperature-programmed mode of 40 $^{\circ}$ C (1 min)–35 $^{\circ}$ C min^{-1} –250 $^{\circ}$ C (35 min).

Results and discussion

Catalyst characterization

XRD analysis

The XRD patterns for MK10, CaO@MK10, MgO@MK10, CaO–MgO@MK10-1.5:1 and CaO–MgO@MK10-1:1.5 samples are displayed in Fig. 1. The characteristic diffraction peaks in the diffractogram of MK10 which occurred at $2\theta = 8.88^{\circ}$, 26.7° , 36.5° and 61.9° were attributed to the crystalline framework of the clay support. However, upon single metal oxide (CaO and MgO) loading on the support, new peaks attributed to CaO (31.6° and 36.8°), Ca(OH)₂ (17.4° and 29.7°), CaSiO₂ (33.3°) and CaAlSiO₂ (41.5°) phases appeared on CaO@MK10's XRD pattern, while new peaks, which were due to the presence of MgO (35.9° , 43.2° and 62.6°) and Mg(OH)₂ (55.1°), appeared on the XRD pattern of MgO@MK10. Both Ca(OH)₂ and Mg(OH)₂ might have formed as a result of reaction between CaO or MgO and atmospheric moisture [20, 22]. When the CaO–MgO supported on MK10, the peaks pointing to CaO and MgO phases were also clearly seen, and their peaks intensities were sharp. Also, the peaks associated with SiO₂ (20.1° , 26.9° , 50.4° and 60.7°), Al₂O₃ (19.8°) CaSiO₂ (75.4°), CaAlSiO₂ (43.3° and 48.6°) phases were detected in the XRD

patterns of the CaO–MgO@MK10 samples, suggesting the synergies between the alkaline earth metal oxides and metal oxides in the support material, which made the composite catalysts sufficiently active in the methanolysis process [4, 19]. It is worthy of note that intensities of peaks in the diffractograms of CaO–MgO@MK10-1.5:1 and CaO–MgO@MK10-1:1.5 samples were identical but the peak ($2\theta = 8.88^{\circ}$) attributed to main feature of MK10 was not found in XRD pattern of CaO–MgO@MK10-1:1.5 due to the impregnation and calcination effects, while the sharp and enhanced peaks of CaO and MgO might probably promote the basicity of CaO–MgO@MK10 catalysts.

Textural and basic properties analysis

The findings of N₂ sorption analysis carried out on MK10, single metal oxide loaded MK10 (CaO@MK10 and MgO@MK10) and mixed metal oxides loaded MK10 (CaO–MgO@MK10-1.5:1 and CaO–MgO@MK10-1:1.5) composites are shown in Fig. 2a and c, indicating that the adsorption isotherms of the samples were type IV with H3 hysteresis loop in line with IUPAC classification which was characteristics of N₂ adsorption on mesoporous materials with slit-shaped pores. The analysis of pore size distribution showed that the pore diameters of the clay and the composite catalysts were within the range of 6 and 22 nm as evidenced in Fig. 2b and d, which reaffirmed mesoporous nature of the solid materials because their average pore diameters are within 2 and 50 nm. The textural attributes (surface area, pore volume and pore size) of the various as-synthesized catalysts were shown in Table 2. The results demonstrated that surface area and pore volume reduced as active ingredients (CaO, MgO or CaO–MgO) were impregnated on the

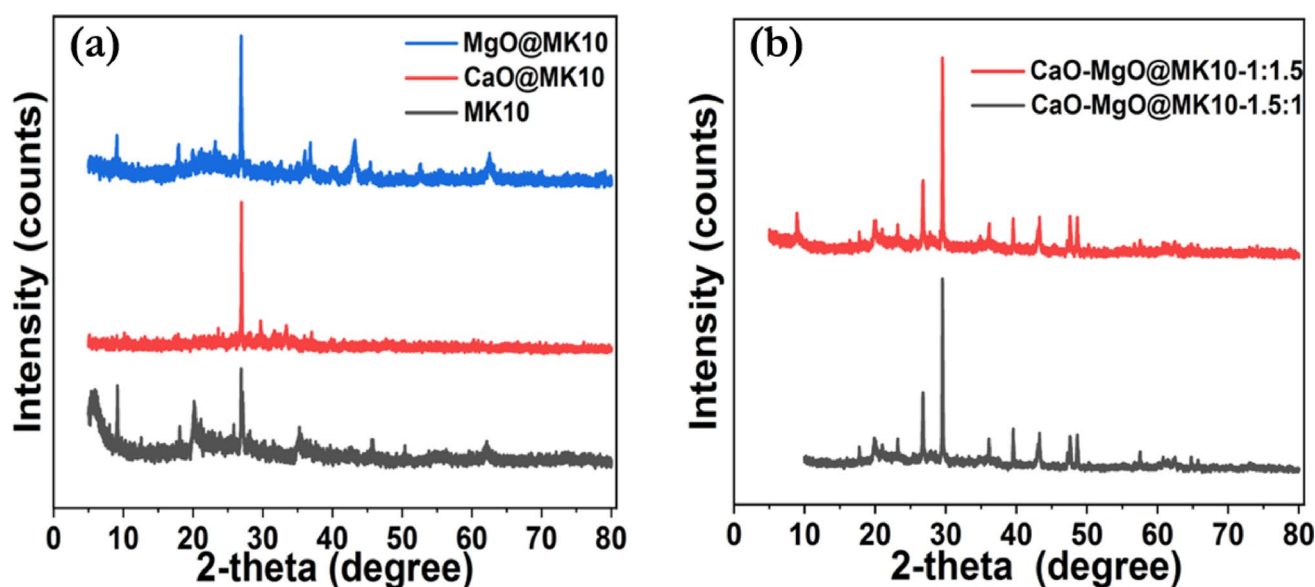
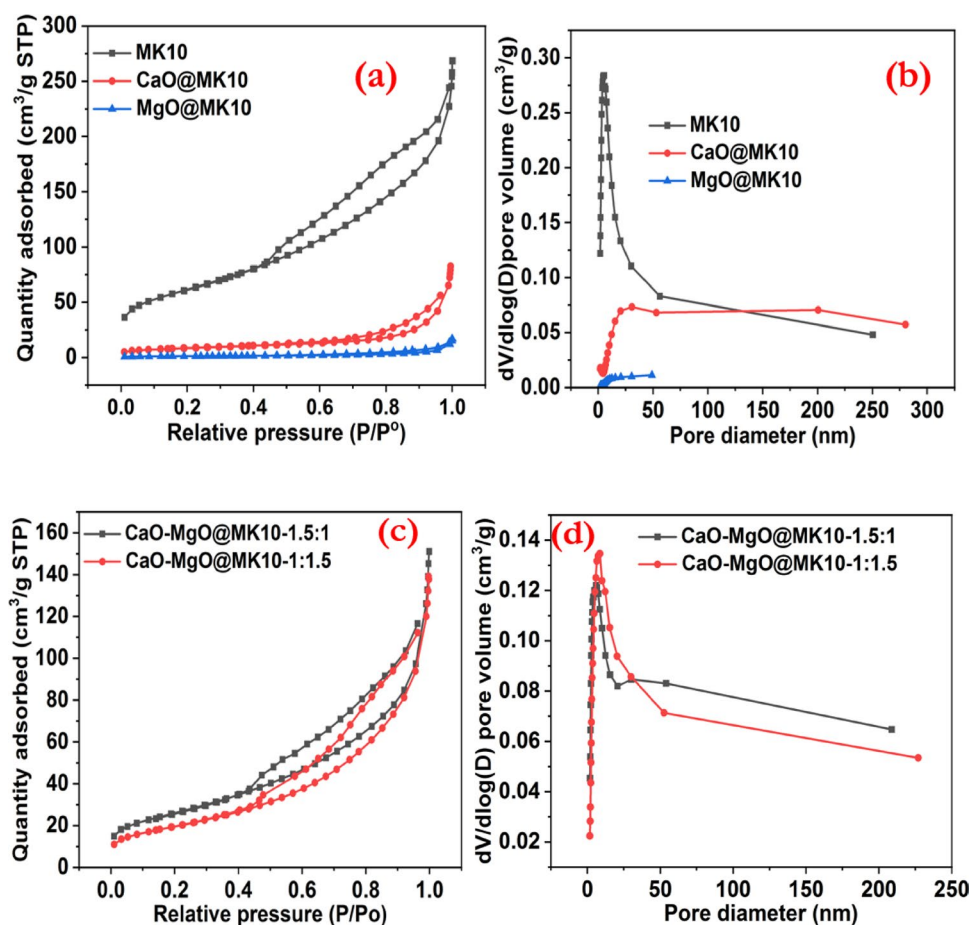


Fig. 1 XRD patterns of a MK10, CaO@MK10 and MgO@MK10 and b CaO–MgO@MK10-1.5:1 and CaO–MgO@MK10-1:1.5

Fig. 2 **a, c** N_2 adsorption-desorption isotherm spectra and **b, d** pore size distribution of MK10, CaO@MK10, MgO@MK10, CaO–MgO@MK10-1.5:1 and CaO–MgO@MK10-1:1.5 catalysts



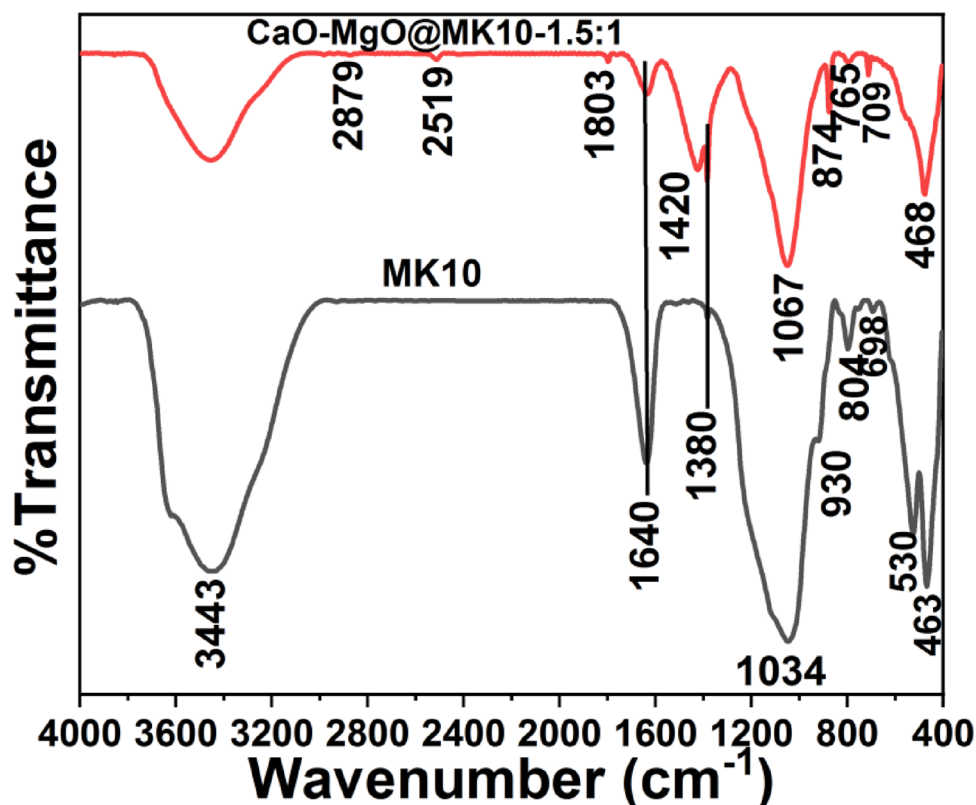
MK10. However, the pore diameters of the resulting composite catalysts were larger than that of the MK10, implying the possible inclusion of the support's mesopores, which led to a reduction in pore volume and specific surface area. This inference aligned with study reported by Olutoye et al. [4] who documented low surface area during BaO loading onto MK10. The surface areas and pore volumes of single metal oxide (CaO or MgO) doped MK10 samples were lowered as compared to CaO–MgO@MK10 composites probably due to the synergies between the two alkaline earth metal oxides which created a porous structure as affirmed by SEM analysis (Fig. 4), while the pore diameters of the CaO@MK10 and MgO@MK10 composites were larger than those of CaO–MgO@MK10 composites, ascribing to possible inclusion of mesopores of the MK10 which in turn reduced its pore diameter and surface area. Similarly, a significant decrease in the surface area and pore volume were reported during impregnation of CaO–CeO₂ onto hydroxyapatite, as documented by Yan et al. [16]. The possibility of the Ca, Mg or Ca–Mg multilayer creation on the MK10 surface during impregnation could not be ignored. Thus, the partial blockage of the pores caused by the multilayer dispersion of the metals reduced the pore volume and surface area [23, 24]. Furthermore, the basic strengths of the as-prepared

composite materials, as evaluated by Hammett indicator method discussed in Sect. 2.3, were much higher than that of the support which indicated the basic properties improvement, making the composites to serve as base catalysts for methanolysis reaction.

^a BET surface area, ^b pore volume, ^c average pore diameter, ^d measured by Hammett method, ^e estimated by Eq. 1.

FTIR analysis

The surface functional groups on support (MK10) and CaO–MgO@MK10-1.5:1 were examined by FTIR spectrophotometer. The FTIR spectra for the two samples are displayed in Fig. 3. The peaks appearance at 3443 cm^{-1} in the spectra of both samples indicated the presence of absorbed moisture and external O–H stretching mode, probably associating with O–H groups present in Ca(OH)₂ and Mg(OH)₂, which could be generated by degradation of nitrates of Ca and Mg followed by their interactions with H₂O [19, 22]. The appearance of peaks at 2879 cm^{-1} and 2519 cm^{-1} in CaO–MgO@MK10-1.5:1 was due to the C–H asymmetric stretching in methyl groups and C–H symmetric stretching in the methylene groups, respectively [4]. Si–O–M⁺ deformation and O–Si–O stretching vibration respectively

Fig. 3 FTIR spectra of MK10 and CaO–MgO@MK10-1.5:1 catalyst**Table 3** Elemental compositions of MK10 and CaO–MgO@MK10-1.5:1 catalyst

Sample	Element compositions (%)								
	Si	Al	O	Na	C	Fe	Ca	Mg	Others
MK10	31.1	4.96	58.1	0.13	–	1.48	0.31	0.69	3.05
CaO–MgO@MK10-1.5:1	33.4	3.72	47.6	0.41	0.95	0.034	7.89	4.03	1.97

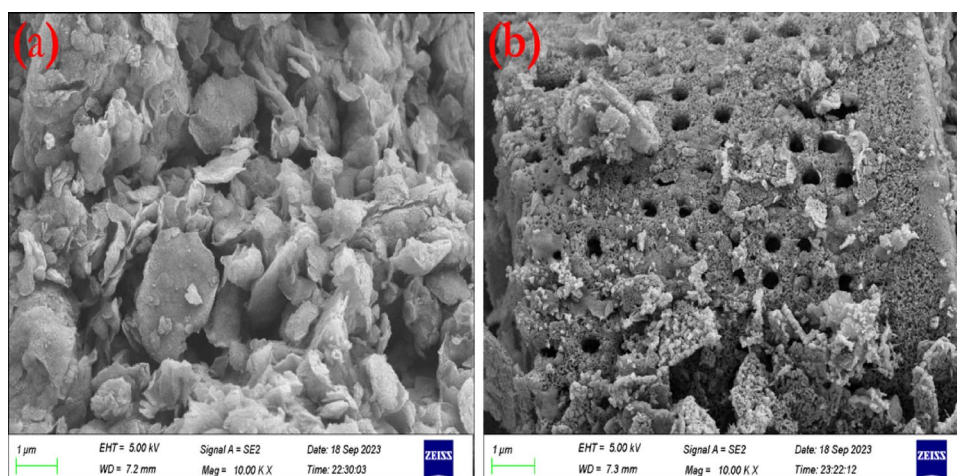
occurred at around 1640 cm^{-1} and 1803 cm^{-1} . Furthermore, the two peaks between 1420 cm^{-1} and 1380 cm^{-1} in the spectrum of CaO–MgO@MK10-1.5:1 catalyst suggested the presence of Ca and Mg groups in the composite catalyst [24]. The broad bands which appeared at 1034 cm^{-1} and 1067 cm^{-1} in the spectra of the support and composite catalyst, respectively were ascribed to the stretching vibration of Si–O–Si, thus affirming the silica presence in both MK10 and Ca–Mg loaded MK10 catalyst as corroborated by XRD result (Fig. 1) and EDX result (Table 3), while the absorption bands below the wavenumber of 1000 cm^{-1} on the spectra of both samples were attributed to either $\text{M}^+\text{-OH}$ or M-O ($\text{M}=\text{Ca}$, Mg or Al) stretching vibration, aligning with some similar reported studies [4, 23, 24]. These findings further proved that the impregnated particles on the clay support in Fig. 3 were CaO and MgO.

SEM-EDX analysis

Figure 4 shows the SEM images of MK10 and CaO–MgO loaded MK10 at Ca–Mg molar ratio of 1.5:1. The support

material exhibited a dried hibiscus flower-like, irregular and rough surface structure. However, upon impregnation of CaO–MgO onto MK10 at 1.5:1 Ca: Mg molar ratio (Fig. 4b), the resulting solid base catalyst showed a flake-like structure with significant numbers of homogeneous layers of pores where there was a good possibility for rapid adsorption of reactants onto catalyst prior to surface reaction. The elemental compositions of MK10 and CaO–MgO@MK10-1.5:1 were presented in Table 3. The clay support mainly consisted of Si, Al, O, Na and some other minor elements like Mg, Ca and Fe. As CaO–MgO was doped with the clay support, the compositions of Ca and Mg noticed on the CaO–MgO@MK10-1.5:1 catalyst's surface increased, thus suggesting successful dispersion of the alkaline earth metals in the clay matrix which promoted basicity of the composite catalyst, thereby enhancing catalytic activity and biodiesel yield.

Fig. 4 SEM micrograms of MK10 and CaO–MgO@MK10-1.5:1 catalyst



Impact of active ingredient loading on biodiesel yield

The values of biodiesel yields achieved using all as-synthesized composites (MK10, CaO @MK10, MgO@MK10, CaO–MgO@MK10-1.5:1 and CaO–MgO@MK10-1:1.5) are listed in Table 2. According to the results, the MK10 offered low biodiesel yield of 18.2% due to the absence of basic sites on its surface which is responsible for shifting the reversible reaction (transesterification) forward. This observation was expected because commercial MK10 surface is relatively acidic [4]. However, a significant increase in biodiesel was noticed with impregnation of single metal oxides, CaO and MgO, on the support (MK10) surface, suggesting enrichment of basic properties of the resulting catalysts. The CaO@MK10 and MgO@MK10 catalysts respectively offered 84.5% and 77.1%, reflecting an approximately similar value of biodiesel yield (83.38%) reported by Olutoye et al. [4] who synthesized biodiesel via methanolysis of WCO with BaO-modified MK10 catalyst. With this comparison, it could be deduced that single alkaline earth oxide supported with MK10 hardly offered biodiesel yield exceeding 90%. Meanwhile, mixed Ca–Mg oxides doped MK10 composites exhibited impressive catalytic performance as CaO–MgO@MK10-1.5:1 and CaO–MgO@MK10-1:1.5 gave 95.2% and 90.6% biodiesel yields, respectively. These observations were attributed to high basicity of the catalysts, corresponding to the presence of CaO and MgO as revealed by both XRD and EDX analyses (Fig. 1; Table 3). The oxygen atoms in the CaO and MgO signified Lewis' base sites, whereas Ca^{2+} and Mg^{2+} represent Lewis' acid sites whereby the high biodiesel yield obtained indicated that the Lewis' base sites served as active sites during the methanolysis process [25].

Furthermore, as evidenced by the biodiesel yield values in Table 2, higher amount of Ca in the composite had significant influence on its activity as Ca^{2+} : Mg^{2+} ratio of 1.5: gave higher yield of biodiesel as compared to that of

1:1.5 Ca^{2+} : Mg^{2+} ratio, which affirmed that CaO is more basic than MgO and important to enhance the basicity of the composite catalysts [7, 11]. However, the MgO presence in the composite was crucial to promote CaO dispersion and to eliminate its agglomeration during calcination or reaction process [4, 11]. The findings presented herein implied that basicity and textural properties played a critical role in catalytic activity. Thus, the CaO–MgO@MK10-1.5:1 catalyst was considered for further investigations in the current study.

Evaluation of optimum transesterification reaction conditions

The whole design matrix coupled with the values of biodiesel yield and S/N ratio from transesterification reaction studies are presented in Table 4. The results indicated that the biodiesel yield was significantly influenced by the variation of transesterification process parameters. The lowest biodiesel yield was obtained to be 49.3% at 70 °C for 5 h with 10:1 CH_3OH /oil molar ratio and 1 wt% CaO–MgO@MK10-1.5:1 loading, whereas the highest biodiesel yield of 94.2% was obtained with 10:1 CH_3OH /oil molar ratio and CaO–MgO@MK10-1.5:1 concentration of 3 wt% at 60 °C for 3 h. These observed results confirmed that the maximum biodiesel yield was not obtained at highest level of each parameter.

Reaction temperature influence

The transesterification temperature effect on biodiesel yield was evaluated by changing its value from 50 to 70 °C. Figure 5a, b (plots of mean of S/N ratio and mean of biodiesel yield against reaction temperature) showed that when the temperature rose from 50 to 60 °C, both the S/N ratio and the biodiesel yield increased but then decreased as the temperature reached 70 °C. These observations, which agreed

Table 4 Taguchi L_9 (3^4) design matrix for biodiesel production process conditions and estimated yields of biodiesel and corresponding S/N ratios

Run No.	Transesterification process factors				Response	
	Temperature, T_T (°C)	Time, t_T (h)	CH ₃ OH/JCO molar ratio, M	Catalyst concentration, C (wt%)	Biodiesel yield (%)	S/N ratio
1	50	3	8:1	1	68.7	36.74
2	50	4	10:1	2	79.1	37.96
3	50	5	12:1	3	70.6	36.98
4	60	3	10:1	3	94.2	39.45
5	60	4	12:1	1	78.5	37.90
6	60	5	8:1	2	59.3	35.46
7	70	3	12:1	2	90.8	39.16
8	70	4	8:1	3	87.1	38.80
9	70	5	10:1	1	49.3	33.86

with the results reported by Tan et al. [21], affirmed the significant influence of temperature on biodiesel production process. Transesterification temperature promotes the reactants diffusion and catalyst particles dispersion, thus affecting the reaction outcome. The increase in temperature also promotes the interactions between the catalyst with H^+ from CH₃OH and mixed oxide catalyst with the alkyl group of the limiting reactant (triglyceride) and fatty acid-generating nucleophile, then rearrangement and proton transfer, leading to high product yield [2, 4,]. The decline in biodiesel yield at 70 °C was caused by gasification of CH₃OH, which lowered the amount of the biodiesel produced while enhancing the byproduct (glycerol) synthesis. Therefore, 60 °C was the optimal reaction temperature.

Reaction time influence

The transesterification of pretreated JCO with CH₃OH was conducted at different reaction durations ranging from 3 to 5 h to study the reaction time impact on the biodiesel yield. Figure 5a, b showed the plots of mean of S/N ratio and mean of biodiesel yield against reaction time, respectively. Therefore, both S/N ratio and biodiesel yield decreased with transesterification duration. At the initial stage of the reaction process, biodiesel production was rapid and finally attained maximum yield in 3 h. In the work reported by Tan et al. [21] on UFO conversion to biodiesel by eggshell-derived CaO catalysts, they concluded that high alcohol concentration and shorter reaction duration shifted the transesterification to equilibrium faster. However, prolong reaction time lowers the biodiesel yield as methanolysis process is a reversible reaction [6]. Thus, 3 h could be said to be optimum reaction duration.

CH₃OH/oil molar ratio influence

Figure 5a, b revealed that both mean of S/N ratio and mean of biodiesel yield rapidly increased as the molar ratio of CH₃OH: JCO rose from 8:1 to 12:1. Generally, high CH₃OH concentration is required to drag the methanolysis forward

to achieve larger biodiesel yield. Hence, a larger molar ratio enhances interaction between the solvent and the oil. However, when the molar ratio of CH₃OH to oil is low, it would have an adverse influence on biodiesel yield. Utilization of limited alcohol during reaction could lower the rate of reaction between alcohol solvent and triglycerides in the oil, which results in incomplete conversion of the limiting reactant to biodiesel, and hence a lower yield. This finding therefore suggested that appropriate CH₃OH concentration would drive the reaction equilibrium to the forward direction, facilitating high biodiesel formation as the optimum molar ratio was 12:1.

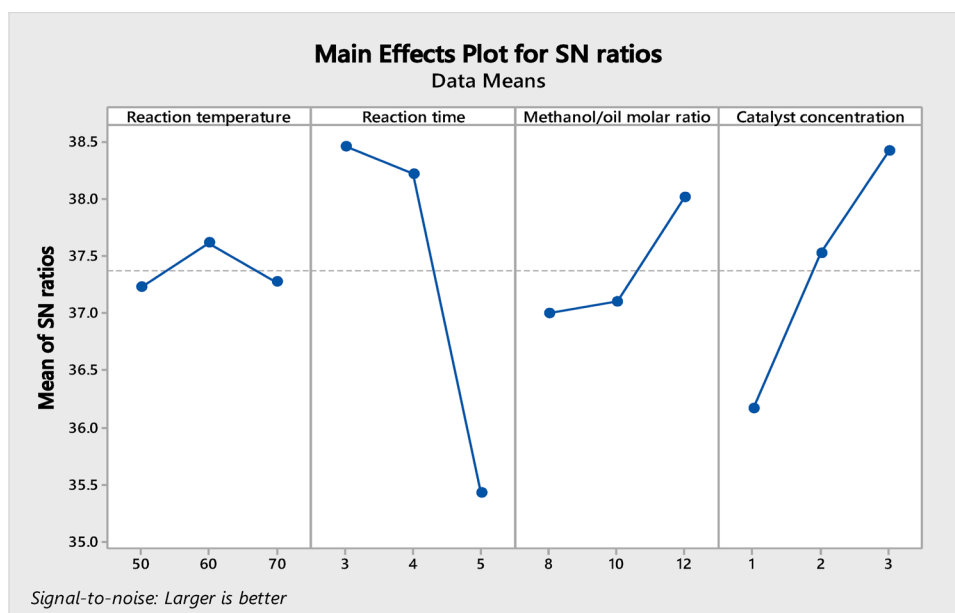
Catalyst concentration influence

The influence of catalyst concentration on the S/N ratio and biodiesel yield is shown in Fig. 5. Increasing the CaO–MgO@MK10-1.5:1 loading from 1 wt% to 3 wt% exhibited a significant change in S/N ratio. This observation indicated that only a specific quantity of catalyst was required to catalyze the methanolysis reaction. At higher catalyst amount, the contact between the CaO–MgO@MK10-1.5:1 composite and the reactants increased as more catalytic active sites were available, thereby favouring biodiesel yield. However, the drop in yield of biodiesel observed at catalyst concentration < 3 wt% was likely owing to the low availability of catalyst active sites, which could drive the reaction faster towards equilibrium [3, 26]. Previous studies, notably Taufiq-Yap et al. [27], Olutoye et al. [4] and Madhuranthakam et al. [28], who used NaOH/Al₂O₃, BMK10 and GO/ZrO₂-SrO as catalysts, obtained similar results. Therefore, optimum catalyst concentration was 3 wt%.

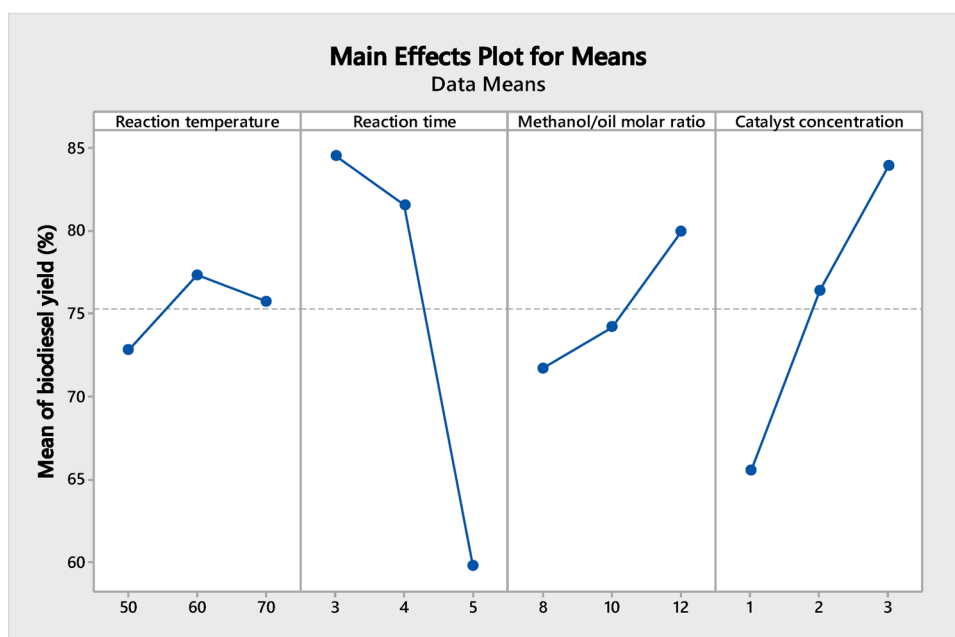
Statistical analysis of variance (ANOVA) for *J. curcas* biodiesel production process parameters

The ANOVA for the regression model for the yield of biodiesel obtained via transesterification of JCO with CH₃OH over CaO–MgO@MK10-1.5:1 catalyst is listed in Table 5. The results consisted of Fischer's statistical value (F-value),

Fig. 5 Response plot for **a** mean of S/N ratios and **b** mean of biodiesel yield against reaction temperature, reaction time, CH₃OH/oil molar ratio and catalyst concentration (wt%)



(a)



(b)

sum of square, p-value and contribution percentage (CP) to evaluate the significance of each influencing factor. The higher F-value implies a larger level of significance [11]. The value of sum of square was used to determine the CP value for individual variable as estimated using Eq. (7). The p-value less than 0.05 represents significant parameter, whereas the p-value greater than 0.05 implies an

insignificant parameter. Table 5 therefore indicated that the extents of influence of the controllable factors on the biodiesel synthesis process were methanolysis time > catalyst concentration > CH₃OH/JCO molar ratio > transesterification temperature.

Table 5 revealed a wide range of CP values from 0.83 to 59.6%, indicating the difference in level of contribution

Table 5 ANOVA for biodiesel production process

Source	DOF	SOS	MS	F-value	p-value	CP (%)
Regression	4	1551.98	388.00	7.50	0.038	
Temperature	1	12.91	12.90	0.25	0.644	0.83
Time	1	925.04	925.04	17.87	0.013	59.60
CH ₃ OH/JCO molar ratio	1	102.51	102.51	1.98	0.232	6.61
Catalyst concentration	1	511.53	511.53	9.88	0.035	32.96
Residual	4	207.05	51.76	—	—	
Total	8	1759.03				

of each independent variable. Time of reaction was found to be the most significant parameter with CP of 59.6%, whereas transesterification temperature appeared to be the least influencing variable with the CP of 0.83%. Comparing the results obtained herein to previously reported studies [2, 11], it could be deduced that the percentage of contribution of the influencing factors to biodiesel production process depended on the feedstock used. The synthesis of *Manilkara zapota* oil biodiesel showed that catalyst concentration contributed largely to the transesterification process with CP of 67%, while time of reaction (CP=1.6%) contributed least to the reaction process [18]. Methanolysis of yellow grease to produce biodiesel showed that catalyst calcination temperature was the most significant parameter at 72.1% contribution followed by catalyst dosage at 17.9% [29].

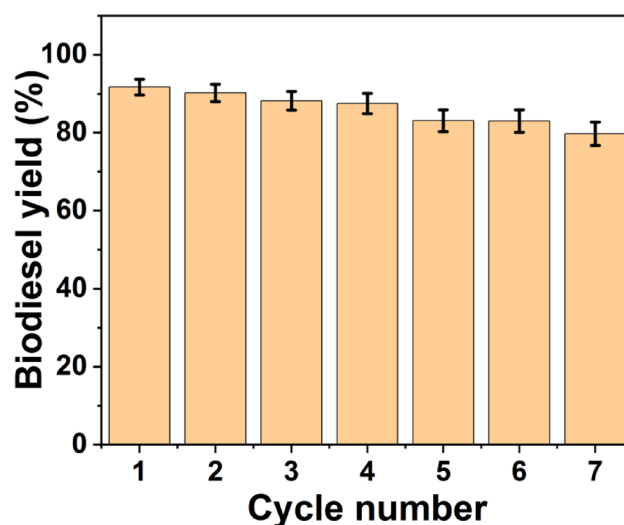
$$CP = \left[\frac{SOS_i}{\sum SOS_i} \right] \times 100\% \quad (i \neq 0) \quad (6)$$

where SOS_i - sum of square of a variable, while $\sum SOS_i$ - total sum of squares of all variables.

Experimental validation under optimum conditions

As confirmed by S/N ratio plots (Fig. 5), the optimized process conditions for biodiesel synthesis from JCO using CaO–MgO@MK10-1.5:1 catalyst were 60 °C, 3 h, 12:1 and 3 wt% for transesterification temperature, methanolysis time, CH₃OH/JCO molar ratio and CaO–MgO@MK10-1.5:1 concentration, respectively, and at these process conditions, further biodiesel experiments were carried out which resulted in average biodiesel yield of $97.2 \pm 0.17\%$. However, the predicted biodiesel yield, which was 95.7%, was estimated by inserting the optimal values of the reaction conditions into Eq. (7) as suggested by Minitab software. Both predicted and observed values of biodiesel agreed with each other with relatively slight difference, thus confirming that statistical optimization through Taguchi approach was effective to accurately predict the biodiesel production from JCO using CaO–MgO@MK10-1.5:1 composite catalyst.

$$Y = 77.0 - 0.147T_T + 12.42t_T + 2.07M - 9.23C \quad (7)$$

**Fig. 6** Reusability study of CaO–MgO@MK10-1.5:1 catalyst under optimal reaction conditions

where Y , T_T , t_T , M and C are biodiesel yield (%), transesterification temperature (°C), transesterification time (h), CH₃OH/JCO molar ratio and catalyst concentration (wt%), respectively.

Catalyst reusability studies

Reusability is a unique attribute of heterogeneous catalyst that makes it superior over homogeneous catalyst and enzymes. However, repetition of reaction cycle using a regenerated catalyst often reveals depreciation in activity of the heterogeneous catalyst. After the spent catalyst was regenerated through the procedures reported in Sect. 2.4, the catalyst reusability test was performed under optimal reaction conditions, as illustrated in Fig. 6, yielding 91.7% and 79.7% biodiesel for the first and seventh cycles, respectively. After fourth cycle, the biodiesel yield was maintained at $\approx 80\%$, indicating that CaO–MgO@MK10-1.5:1 was relatively stable, retaining its activity even after seven cycles with minimal leaching of <15%. This was due to a reduction in active sites on the catalyst surface caused by adsorbed unreacted reactants and intermediates [3]. Comparing with other composite catalysts such as BMK10 [4], CaO/zeolite [24], MgO/Fe₂O₃–SiO₂ [30] and GO/ZrO–SrO [28], CaO–MgO@

MK10-1.5:1 catalyst offered high biodiesel yield after last cycle, and the trend that catalytic activity declined slightly from first cycle to fourth cycle and sustained stability in the subsequent cycles indicated promising industrial application potential of CaO–MgO@MK10-1.5:1 catalyst.

Biodiesel characteristics evaluation

Biodiesel physicochemical attributes

Table 6 lists the physicochemical properties of the biodiesel sample prepared under optimal conditions, and the results showed that each of the fuel parameters concurred with ASTM D6751 standard values, demonstrating that the obtained biodiesel sample was of high quality and suitable as a substitute for fossil diesel. More importantly, the considerable drop in relative density and kinematic viscosity following JCO conversion to biodiesel confirmed the efficacy of transesterification of JCO with CH₃OH over the CaO–MgO@MK10-1.5:1 catalyst. The safety of the optimal produced biodiesel is said to be guaranteed during transportation and storage due to its high flash point which was far greater than that of fossil diesel [2, 31]. Furthermore, the cold flow properties seemed to possess very good cold flow attributes, as confirmed by the cloud point and pour point values presented in Table 6 which suggested the suitability of the produced biodiesel in cold environment [32]. Moreover, acid value obtained through titration technique fell within EN 14,214 standard, which suggested that the prepared biodiesel could be utilized in diesel engines without causing corrosion or deposits.

Methyl esters content analysis

Table 7 showed the retention times and compositions of various methyl esters contained in the biodiesel synthesized at optimum reaction conditions. The analysis confirmed the existence of three saturated methyl esters with a total composition of 26.68%, as well as nine unsaturated methyl esters with a total composition of 71.17% in the optimal biodiesel sample. Similar findings were also reported by previous researchers: Betiku et al. [33], Anwar et al. [34], Iweka et al. [35] and Alagar et al. [36] who utilized Kariya seed oil (43.1% saturated and 56.9%), Karanja seed oil (22.4% saturated and 77.6% unsaturated), yellow oleander seed oil (25.2% saturated and 74.8% unsaturated) and crude rubber seed oil (18.9 saturated and 80.5% unsaturated) as non-edible biodiesel feedstocks, respectively. The FAME contents in the biodiesel produced in the present study was 97.85% which exceeded 96.5% (European standard EN 14214 for biodiesel), thus indicating that biodiesel produced from *J. curcas* oil via the methanolysis with CaO–MgO@

Table 6 Physicochemical attributes of synthesized optimal JCO-biodiesel in relation to the ASTM standard

Property	Unit	Produced JCO-B	ASTM D6751	ASTM test
Kinematic viscosity @ 25 °C	mm ² /s	4.97	1.9–6.0	D445
Acid value	mg KOH/g	0.43	≤ 0.5	–
Flash point	°C	171	≥ 130	D-93
Pour point	°C	+7.5	–15 to 10	D2500
Cloud point	°C	+8	–3 to 12	D2500
Relative density @ 25 °C		0.884	0.86–0.90	D4052

Table 7 Methyl esters profile of the prepared biodiesel under optimal conditions

Detected compounds	Retention time (min)	Composition (%)
<i>Saturated methyl ester (SME)</i>		
Methyl palmitate	12.93	13.45
Methyl stearate	14.85	13.11
Methyl arachidate	16.73	0.12
Total SME composition		26.68
<i>Unsaturated methyl ester (USME)</i>		
Methyl palmitoleate	13.19	0.79
Methyl oleate	15.10	33.28
Methyl linoleate	15.60	32.20
Methyl linolenate	16.24	0.12
Methyl eicosenoate	17.01	0.06
Methyl 11, 14-eicosadienoate	20.46	1.03
Methyl 5, 8, 11-eicosatrienoate	24.78	0.72
Methyl arachidonate	25.76	1.84
Methyl eicosapentenoate	27.56	1.07
Total USME composition		71.17
Others		2.15

MK10-1.5:1 catalyst could be used in diesel engine in lieu of a fossil diesel.

Comparison between CaO–MgO@MK10- 1.5 : 1 and previously reported catalysts

The catalytic efficacy of the CaO–MgO@MK10-1.5:1 composite in terms of FAME content was compared to previously use heterogeneous catalysts for biodiesel synthesis from bio-oil, as shown in Table 8. The CaO–MgO@MK10-1.5:1 exhibited excellent catalytic activity by offering FAME content of 97.85% at 60 °C for 3 h with 3 wt% catalyst concentration and 12:1 CH₃OH/JCO molar ratio. According to Tan et al. [21], heterogeneously catalyzed transesterification process that offered FAME content ≥ 96.5% (EN 14214 standard for biodiesel) reflects catalytic potential of the catalyst used for triglyceride conversion to biodiesel. Since the FAME content obtained herein exceeded 96.5%, it could be

Table 8 Comparison of the FAME yield using various heterogeneous base catalysts

Catalyst	Transesterification reaction conditions				FAME yield (%)	References
	Temperature (°C)	time (h)	CH ₃ OH/oil molar ratio	Catalyst concentration (wt%)		
BMK10	150	5.0	12:1	3.5	83.38	[4]
ZnO/Ag nanoparticles	60	1	10:1	10	97	□
Clay-Na ₂ CO ₃	60	1.5	12:1	2	94.7	□
Nano CaO	60	2	12:1	2.5	94	□
Na ₂ O/carbon nanotubes	65	3	20:1	3	97	□
GO/ZrO-SrO	120	1.5	4:1	0.5	91	□
MgO/MgAl ₂ O ₄ nano	110	3	12:1	3	95.7	□
Zn-doped CaO nano	55	1.33	9:1	6	89	□
Zeolite supported CaO	69.1	3.97	9.7:1	2.1	93.7	□
CaO–MgO@MK10-1.5:1	60	3	12:1	3	97.85	Current study

deduced that CaO–MgO@MK10-1.5:1 was efficient for the transesterification process, indicating that it was a promising solid catalyst for the bio-oil conversion to biodiesel via methanolysis process, especially when compared to clay-Na₂CO₃ (94.7%) [37], Zn-doped CaO nano (89%) [38], zeolite supported CaO (93.7%) [39] and Ba-doped MK10 (BMK10) (83.38%) [4].

Conclusions

The methanolysis of JCO with CaO–MgO@MK10-1.5:1 as catalyst was studied. Findings obtained indicated that the utilization of modified natural aluminosilicate material as heterogeneous catalyst was proven to be efficient toward methanolysis of JCO and capable to give $97.2 \pm 0.17\%$ of biodiesel yield at 3 wt% catalyst loading, time of reaction of 3 h, 60 °C methanolysis temperature and 12:1 CH₃OH/oil molar ratio. The influences of the various parameters on the reaction process were discussed. The slight decrease in catalytic activity after seven reaction cycles was noticed, indicating that organic residues were contained in the catalyst even after regeneration. The properties of the biodiesel prepared under optimal reaction conditions aligned with both ASTM D6751 and EN 14,214 standards. Although the CaO–MgO@MK10-1.5:1 composite exhibited an excellent catalytic activity and was relatively stable throughout multiple runs, no attention was given to the conversion of high FFA feedstock via single-step transesterification process. With this unending research that is being carried out on this limitation, we have no doubt that our prepared base catalyst would contribute to enhance the performance of nanoparticles functionalized solids in biodiesel production process.

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Data availability No datasets were generated or analysed during the current study.

Declarations

Conflict of interest No conflict of interest.

Ethical approval The research involved no human participants and/or animals.

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