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Research Article

Reusable Catalyst of KF/Mg-Al Layered Double for Biodiesel Conversion and Optimization using Bohn-Behnken Design

Totok Eka Suharto[1,*], Fethi Kooli[2], Sheikh Ahmad Izaddin Sheikh Mohd Ghazali[3], Is Fatimah[4,*]

[1]*Department of Chemical Engineering, Faculty of Industrial Technology, Universitas Ahmad Dahlan, Kampus 4, Jl. Ringroad Selatan, Kragilan, Yogyakarta, Indonesia.*
[2]*Department of Chemistry, Faculty of Science, Islamic University of Madinah, Al-Madinah Al-Munawwarah 42351, Saudi Arabia.*
[3]*Universiti Teknologi MARA Negeri Sembilan - Kampus Kuala Pilah, Kuala Pilah, Negeri Sembilan, Malaysia.*
[4]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Islam Indonesia, Kampus Terpadu UII, Jl. Kaliurang Km 14, Sleman, Yogyakarta, Indonesia.*

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Abstract

This work aimed to synthesize a reusable catalyst of KF/Mg-Al layered double hydroxide (KF/LDH) for a microwave-assisted biodiesel conversion from rice bran oil (RBO). The LDH was synthesized by co-precipitation method of Mg and Al precursors with additional surfactant of cetyl trimethyl ammonium followed by hydrothermal method, for furthermore, an impregnation procedure was applied to combine KF with LDH by using impregnation method. Instrumental analysis of materials was performed by XRD, gas sorption analysis, SEM-EDX, TEM and XPS method. Effect of KF loading onto LDH on the specific surface area and solid basicity was also studied. From the characterization by XRD, it can be concluded that the impregnation increased specific surface area of LDH without any structural destruction, which was also confirmed by the lattice fringe comparison by HRTEM analysis and surface analysis by XPS. The specific surface area enhancement is in line with the increasing solid basicity which directly enhanced the catalytic conversion of RBO into biodiesel. Statistical optimization of the use of KF/LDH was conducted by response surface methodology of Box-Behnken Design for the range of 2–4 g/100 mL of catalyst dose, 3–8 of the methanol to oil ratio, and 10–30 min of reaction time. It was revealed that all factors are significantly affect the yield. The KF/LDH catalyst is also reusable as it does not loss the activity until 5th cycles.

Keywords: Biodiesel; Microwave-assisted reaction; Layered Double Hydroxides; Basic catalyst

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1. Introduction

World's demand on energy consumption forces many explorations for renewable energy resource, and among various possible sources, biodiesel is the most reasonable choice by many economic reasons. The development of biodiesel industrialization itself considers the low-cost and sustainable production so many intensifications procedures such as ultrasound-assisted conversion, microwave-assisted conversion or enzymatic system were developed [1,2]. In term of fast and biodiesel conversion, heterogeneous

* Corresponding Author.
Email: totok.suharto@che.uad.ac.id (T.E. Suharto); isfatimah@uii.ac.id (I. Fatimah)

catalyzed conversion has been well-known as effective procedure regarding to some advantageous, such as the easy in separation and minimizing consumable catalyst (NaOH) [3–5]. Among various solid base catalysts, layered double hydroxides (LDHs) are attractive materials got intensive consideration due to their easy in preparation and tunable properties. As the structure is a layer structure, it is easily manipulated to get the functional properties for certain potential applications [6,7].

In term of basic catalyst in biodiesel production, the functionalization can be achieved by enhancement of its basicity via supporting super basic compounds, one of these is by KF supporting treatment. Previous research reported an excellent catalytic activity of KF modification to Ca-Al LDHs [8]. Similarly, KF-modified commercial hydrotalcite of sorbacite for biodiesel production was also reported [9]. However, from various studies, the physicochemical performance of material, mainly the basicity of the solid play role in the catalysis effectivity, and it is related with the preparation procedure, process and optimization. A strategy to prepare basic solid catalyst via KF-modification onto Mg-Al LDHs was conducted in this research. In order to increase the specific surface area of LDHs, hydrothermal-assisted synthesis was attempted before KF impregnation.

Even though some studies on KF-modified LDHs have been conducted, to our knowledge, the combination of hydrothermal synthesized Mg-Al LDHs and its modification with KF to provide the sufficient specific surface area and basicity is the new idea and novelty of the work in frame of enhancement the catalyst stability. Furthermore, to proof the attempted characteristics, the optimization of catalyst use, time-effective process, and moreover reusability of catalysts are important issues to be studied. Instrumental analyses on catalyst feature utilizing XPS and catalyst stability using XRD analysis are important progresses on heterogeneous catalysis research. Intensification of biodiesel production via microwave-assisted reaction is a selected procedure for time-effectivity. The participation of intensive collision accelerated by microwave has been widely reported over various catalysts [10]. Based on these backgrounds, this research is aimed to study physicochemical characteristic of KF-modified Mg-Al LDH prepared by hydrothermal synthesis and the optimization study in microwave-assisted conversion of biodiesel using statistical optimization. Considering the powerful response surface methodology by Box-Behnken Design (BBD), this statistical method was applied for optimization.

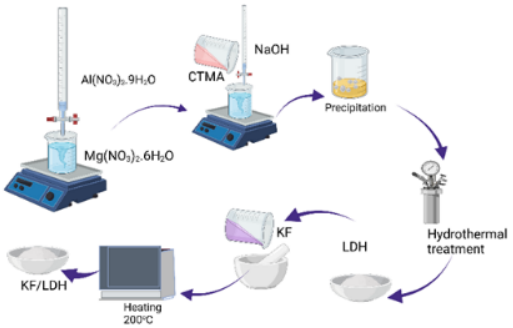


Figure 1. Schematic representation of KF/LDH.

2. Materials and Methods

2.1 Materials

Materials used in this research consist of $Al(NO_3)_3.9H_2O$, $Mg(NO_3)_2.6H_2O$, cetyl trimethyl ammonium bromide (CTMA), methanol, sodium hydroxide, n-butylamine, and citric acid, were purchased from Merck (Germany), and utilized without any further purification. Rice bran oil (RBO) was produced by Indofood Tbk (Indonesia), was utilized without purification.

2.2 Synthesis of Mg-Al Layered Double Hydroxides

Mg-Al layered double hydroxides (furthermore called as LDH) was prepared by the modified coprecipitation method based on previous researches [11,12] on the Mg/Al ratio of 2:1. The solution of magnesium nitrate hexahydrate was mixed with aluminum nitrate nonahydrate solution, and subsequently, the solution of CTMA at 2% v/v was added. The next step was the solution of sodium hydroxide added droply and under stirring until pH of the solution = 10±0.5 with the speed of the addition of 4 mL/min. The gel obtained from these steps was transferred into a sealed Teflon-lined autoclave for hydrothermal treatment at a temperature of 110 °C overnight. The material was dried in oven at 90 °C to obtain LDH. Modification to LDH with KF to get KF/LDH was conducted by mixing LDH powder with KF powder at KF content of 10 %wt. followed by grinding at room temperature for 1 h. The obtained powder was then heated at 200 °C for 2 h. Figure 1 represents the scheme of LDH and KF/LDH preparation.

Physicochemical characters of the materials were studied by X-ray diffraction (XRD), scanning electron microscope-energy dispersive

X-ray (SEM-EDS), transmission electron microscope (TEM), and X-ray photoelectron spectroscopy (XPS) analyses. In addition, the solid basicity of materials was measured by citric acid back titration method. A Shimadzu XRD X6000 diffractometer (Tokyo, Japan) was employed for XRD analysis on a Ni-filtered Cu-Kα radiation (λ = 0.154060 nm) recorded at the range of 2–70°. For surface morphology and elemental analysis studies, SEM-EDS (Phenom-X; Philadelphia, US) were utilized, meanwhile TEM images were taken on JEOL instrument. TEM was operated at the applied voltage of 200 kV, and a monochromatic Al-Kα radiation with a photon energy of 1486.6±0.2 eV. The sample was degassed at the pressure below 10^{-8} Pa for 4 h before analysis. Surface analysis of XPS was performed on V.G. Scientific ESKALAB MKI microscope (Tokyo, Japan). For surface basicity, in principle, the samples were mixed with an excess acetic acid solution and stirred overnight. The unadsorbed citric acid was determined by titration using NaOH as a base standard solution. The solid basicity was measured as the mol equivalent of NaOH per mass of sample.

2.3 Catalytic Activity Testing

Catalytic activity of KF/LDH was examined in biodiesel conversion from rice bran oil (RBO) using a batch reaction system. For each reaction, RBO in mixture with methanol and catalyst was heated in a microwave-assisted method. Microwave-irradiated reaction was executed in a commercial microwave oven (2.45 GHz). Furthermore, the quantitative analysis of the product was evaluated using gas chromatography-mass spectrometry (GC-MS). A Shimadzu GC-MS instrument equipped with the HP-5MS 5% (phenyl methyl siloxane) capillary column (30 m × 250 μm i.d., 0.25 μm film thickness) as fixed phase and a spilt injector and FID detector was employed for analysis. As the carrier gas, helium with an average velocity of 37 cm/sec at 200 °C was employed. The yield (%) was calculated based on following Equation (1):

$$Yield(\%) = \frac{mass\ of\ extracted\ biodiesel(g)}{mass\ of\ TBO(g)} \times 100\% \quad (1)$$

The composition of methyl ester in the biodiesel was based on the peak area of identified component refer to MS peaks compared to the peak area of standard methyl esters.

The initial study was the comparison between microwave irradiation and Reflux method, and in advance, optimization of microwave-assisted reaction was set up in reference to the Box-Behnken Design (BBD) of the Response Surface Methodology (RSM). The varied parameters selected for optimization were time of reaction (X_1), methanol-to-RBO volume ratio time (X_2), and catalyst dose (X_3). The output of data was yield (%) calculated based on the quantitative amount of methyl ester produced in the reaction. The parameters as the independent variables were set to the low, middle, and high levels as shown in Table 1.

Each variable was coded using a coding scheme to denote the level of the factor among three potential levels; −1 indicated the lower level, 0 indicated the medium level, and +1 indicated the higher level. Minitab 16 software (version 6.0) was utilized to carry out the regression analysis and to analyze the constructed data obtained from the preliminary experiments.

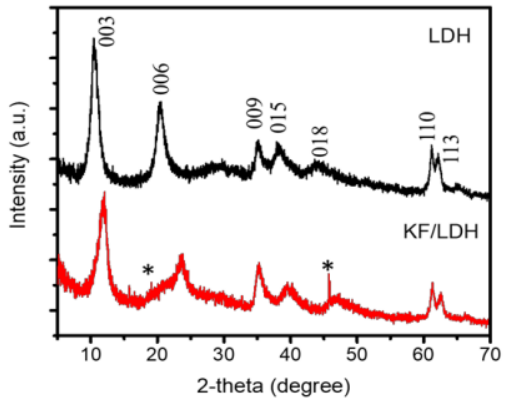


Figure 2. XRD patterns of LDH and KF/LDH.

Table 1. The chosen parameters selected for biodiesel conversion.

Experimental factors	Symbol	Levels		
		Level (−)	Level (0)	Level (+)
Time of reaction (min)	X_1	10	20	30
Methanol to RBO ratio	X_2	3	5.5	8
Catalyst (g/100 mL)	X_3	2	3	4

3. Results and Discussion

3.1 Characterization of Materials

Initial confirmation on LDH formation and the effect of KF modification was by XRD analysis. Figure 2 exhibits the reflections of LDH and KF/LDH. It is seen that both samples show the characteristic peaks of (003), (006), (009), (015), (018), (110), and (113) that are associated with LDH structure [9,10,13]. It is no disappeared peak after modification with KF, moreover, there are two additional peaks at around 19.8° and 45.6° corresponding to the presence of KF [14]. In more detail, it is seen that KF modification shifted the (003) and (006) reflections to higher angle that imply the reduced basal spacing of d_{003} and d_{006} of LDH structure. From the calculated on the analysis values obtained basal spacing d_{003} was changed from 7.70 Å into 7.55 Å, and d_{006} was decreased from 3.82 Å to 3.80 Å.

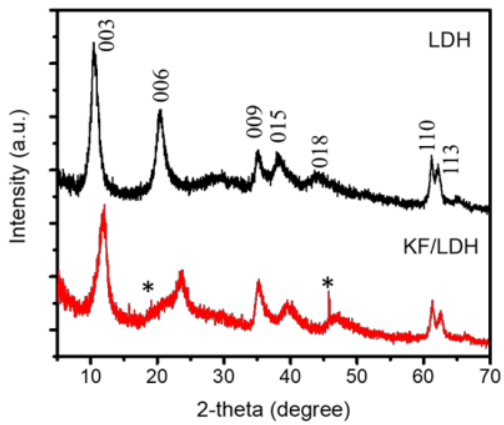


Figure 2. XRD patterns of LDH and KF/LDH.

These changes are confirmed by the HRTEM analysis presented in Figure 3. Even though a layered structure is maintained by KF modification as can be seen from Figure 3(a) and Figure 3(b), the HRTEM spots represents the lattice fringes associated with d_{003} from both samples. The lattice fringes spaces with distance of 0.77 nm and 0.76 nm of LDH and KF/LDH are associated with the partial change of basal spacing d_{003} as identified by XRD. From both XRD and TEM analysis, it is conclusively confirmed that there is inappreciable destructurization, but it is associated with

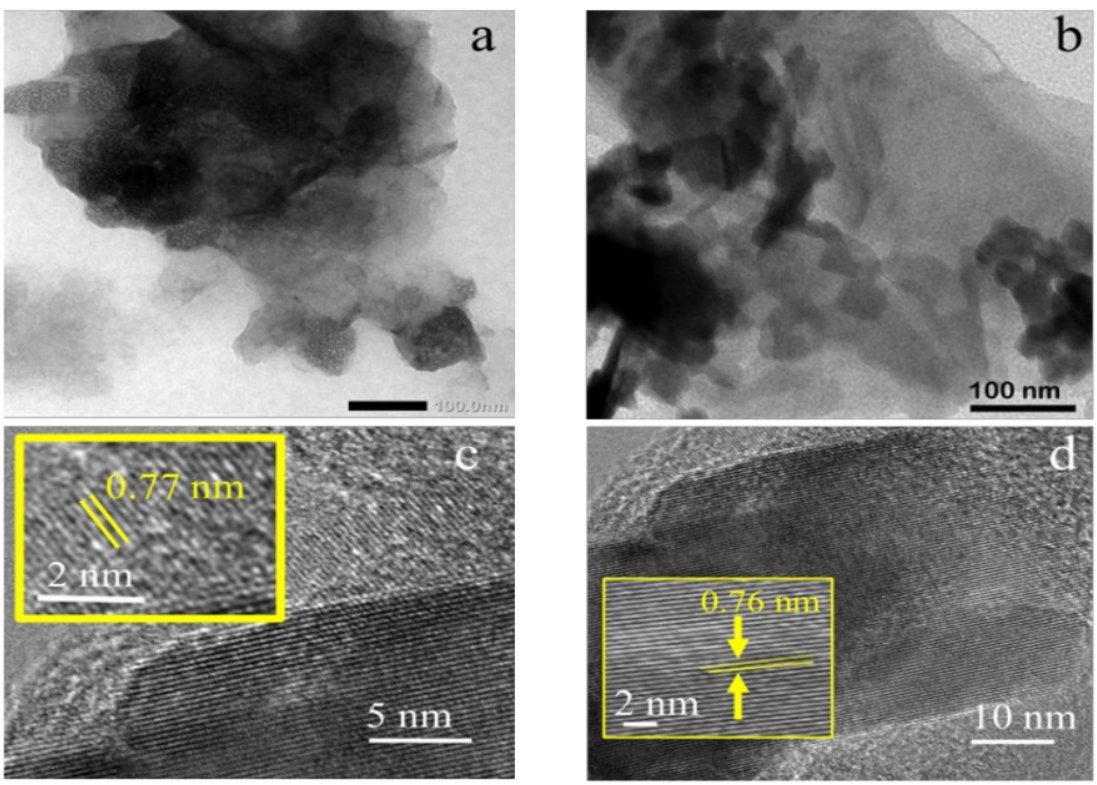


Figure 3. (a-b) TEM images of LDH and KF/LDH and (c-d) HRTEM image of LDH and KF/LDH.

anion balance in the interlayer space. Similar phenomenon was found as the interlayer modification of LDH applied by using glutamate and other surfactants, as well as calcination procedure to remove water from the structure [15–17].

The inappreciable change of the structure is also confirmed by the SEM-EDX analysis with images presented in Figure 4, and the elemental analysis tabulated in Table 2. SEM images represent the characteristic appearance of LDH with a flaky structure of surface. Even though the percentages are less than 10% which was set up in the synthesis, elemental analysis demonstrated the presence of KF as identified by K and F components. The lower percentage may be caused by the loss amount by thermal treatment during preparation.

Table 2. Results of elemental analysis by using EDX.

Element (%wt)	LDH	KF/LDH
O	74.37	51.75
Mg	12.20	24.1
Al	5.36	7.59
Na	0.63	0.53
C	8.23	4.51
K	n.d	4.55
F	n.d	6.50

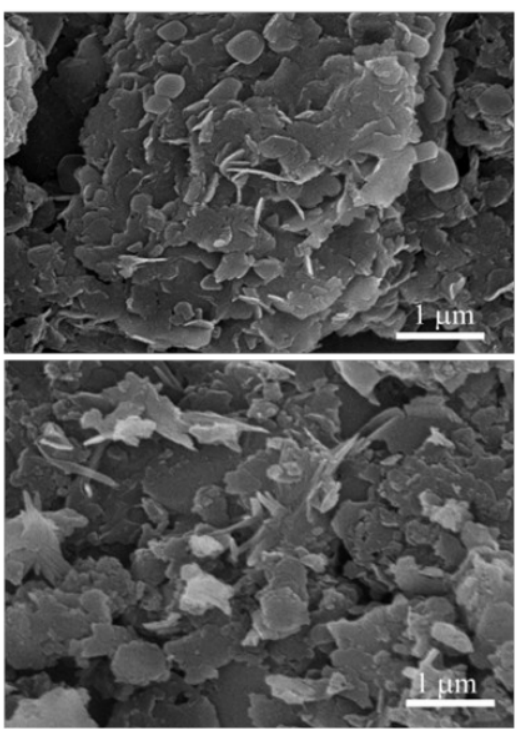


Figure 4. SEM image of (a) LDH and (b) KF/LDH.

The XPS analysis shows the survey spectra of LDH and KF/LDH in Figure 5. It is seen that the spectra expressed some peaks associated with the elements in materials consist of Al 2p at 74.31 eV and Mg 2p at 50.29 eV as main component in LDH structure, beside of O 1s peak at around 530 eV. After was modified with KF, additional peaks are exhibited at 287

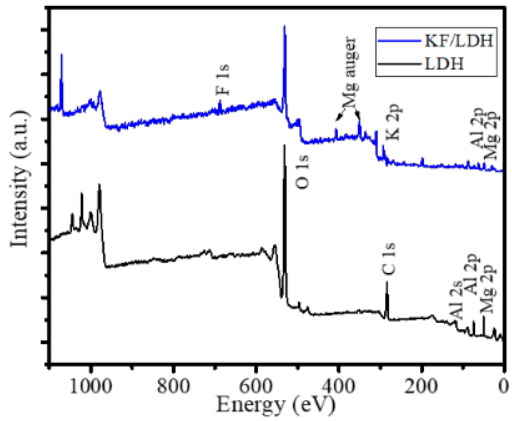
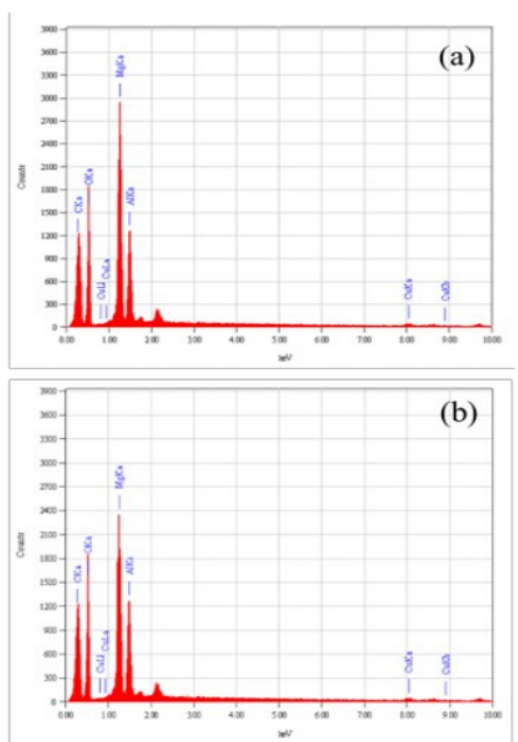


Figure 5. XPS spectra of LDH and KF/LDH.



eV which is associated with K 2p binding energy and at 687 eV which assigned as F 1s peak [18,19]. In addition, it is seen that the main components peaks are still exist. Particularly by the intensity, Mg/Al ratio is about 1.98, near to 2.0 as the set ratio in the synthesis. Conclusively, there is no such significant change of LDH's structure after KF modification.

The specific surface area of LDH and KF/LDH was determined based on gas sorption analysis with adsorption-desorption isotherm presented in Figure 6, and the calculated parameters are listed in Table 3. With a similar Mg/Al ratio, the obtained BET specific surface area from this work (72.8 m^2/g) is higher compared to was synthesized by previous work (50.6 m^2/g) [20], but smaller compared to another work (365 m^2/g) [21]. It can be notified that the parameters were influenced by Mg/Al and the synthesis method [21,22]. In addition, the KF treatment increased either the specific surface area or pore volume of LDH. These evolutions suggest that there is a crucial effect of anionic and cationic interaction to the surface of LDH, as also confirmed by the pore distribution in Figure 6(b). A shifting of dominant pore within the micropores and mesoporous ranges is associated with the isotherm curve in Figure 6(a). Both samples show a H2 type hysteresis loop between 0.5 and 1.0 pressure range, which is associated with the mesoporous structure of pores with the ink bottle type characteristics. The impregnated potassium and fluoride ions contribute to influence the cationic-anionic interaction forced to the interlamellar structures or a formation of mesopores from the layered

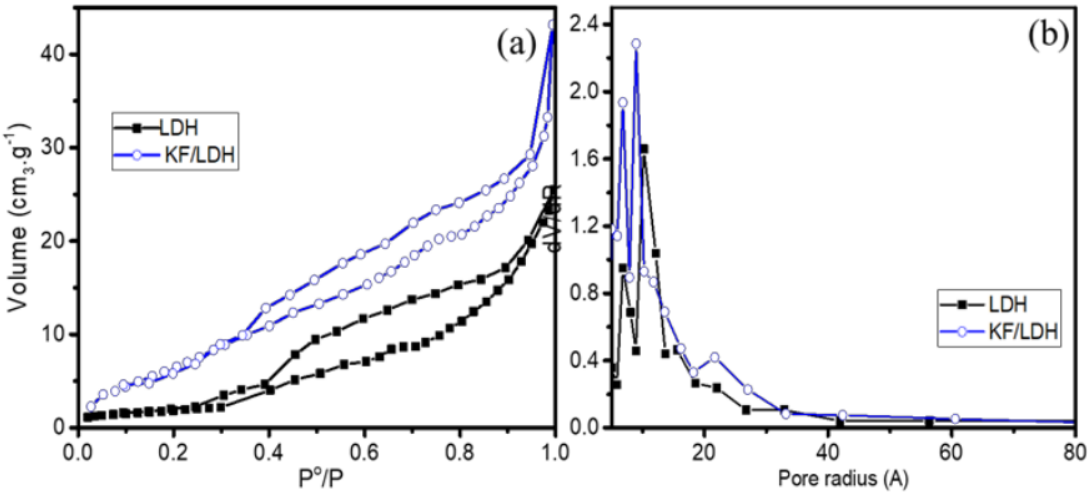


Figure 6. (a) Adsorption-desorption profile, and (b) Pore size distribution of LDH and KF/LDH.

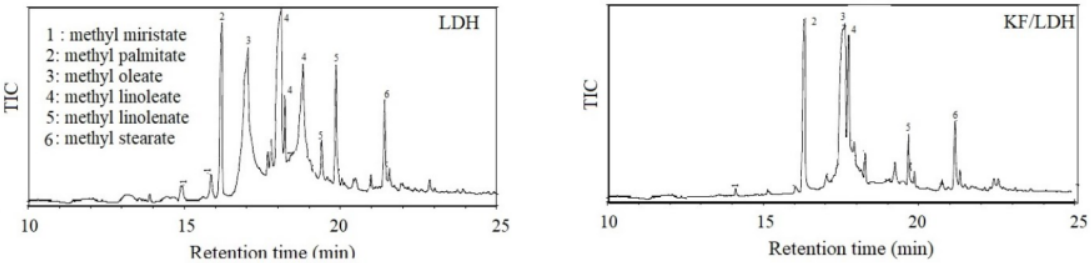


Figure 7. GC-MS profile of biodiesel produced over LDH and KF/LDH.

Table 3. Surface profile parameters and surface acidity data of materials.

Sample	BET specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore radius (Å)	Surface basicity (mmol NaOH/g)
LDH	72.8	0.066	12.2	4.4×10^{-3}
KF/LDH	81.5	0.079	15.6	5.3×10^{-3}

structures [23]. Additionally, the KF impregnation improved the surface basicity from about 4.4×10^{-3} to 5.3×10^{-3} mmol NaOH/g.

The initial study on the comparison between LDH and KF/LDH catalyst for microwave-assisted conversion of RBO to biodiesel was examined by GC-MS analysis. The yield and compositions are presented in Table 4. It is seen that the appreciable yield from 85.6 % by using LDH to be 99.9% yield over KF/LDH was achieved. In more detail, the major components are oleic, linoleic, and linolenic methyl ester similar with previous study, as also presented by the GC-MS analysis results presented in Figure 7 and Table 4 [24]. Here the higher yield respects to the presence of more basic sites and specific surface area on KF/LDH surface contributed to the faster adsorption-desorption which support transesterification mechanism, as hypothesized in this research.

From the yield, reaction condition, and time required for the reaction, it is conclusively obtained that KF/LDH by microwave-irradiation method gave quite high result compared to oth-

Table 4. The yield and average composition of fatty acid methyl ester in produced biodiesel by LDH and KF/LDH catalysts [Condition: irradiation: 30 min; catalyst: 3 g/100 mL; methanol/RBO = 8).

Compound	LDH		KF/LDH	
	Composition (%)	Yield (%)	Composition (%)	Yield (%)
Palmitic acid methyl ester	4.2		1.5	
Oleic acid methyl ester	43.9		46.6	
Linoleic acid methyl ester	38.1	85.6	39.1	99.9
Linolenic acid methyl ester	8.3		7.8	
Stearic acid methyl ester	5.2		4.8	

Table 5. Comparison on catalytic activity of related Mg/Al LDH catalyst for biodiesel production.

Catalyst	Remark	Maximum/optimum yield (Time of reaction)	Ref.
MgAl hydrotalcite	Mg/Al ratio of 3:1, oil resource: waste cooking oil, catalyst of 5% wt., methanol to oil ratio of 30:1, time: 24 h.	87.2 (24 h)	[25]
KF/Ca−Mg−Al hydrotalcite	KF/Ca−Mg−Al hydrotalcite (2.2:0.8:1 Ca/Mg/Al; methanol: palm oil = 12:1, time 10 min	99 (10 min)	[26]
K^+ Modified MgAl-Hydrotalcites	Catalyst loading was 2 wt; methanol/rapeseed oil molar ratio of 12:1, and reaction at 60 °C over 1 h.	99 (5 min)	[27]
KF/Ca-Mg-Al Hydrotalcite	Reaction at 68 °C, with 12:1 methanol/palm oil molar ratio, and 5% (wt/wt oil) catalyst amount.	>90 (10 min)	[26]
H_2SO_4	Microwave-assisted reaction for 60 min with KOH and methanol of 60%	95.4 (60 min)	[28]
Mg/AL LDH modified with Li	MgAl was modified with Li at 40% wt. The reaction for 8H and 10% catalyst gave 90% yield. Temperature of reaction was 55-75 °C and methanol to -oil ratio (from 30:1 to 12:1).	90 (8h)	[29]

er catalyst. The comparison between this work and other similar previous works are listed in Table 5 [25–29]. Refer to Table 5, the obtained yield in this work is higher compared to the use of H_2SO_4 as homogeneous catalyst, and consumed less time of reaction in comparison with other use of LDH by conventional heating.

3.2 Statistical Optimization

For application purpose, the optimization of catalytic activity of KF/LDH was conducted based on RSM using BBD for selected influential parameters. With reference to the catalytic mechanism, the parameters of the ZnO content, catalyst dosage, methanol-to-oil ratio, and time of reaction were chosen. Table 6 lists the yield values at the varied conditions, and Table 7 lists ANOVA results for full-factor analysis.

The determination coefficient, or R^2, of 0.952 indicates that the model could be used as a predictor of the response. Based on the multiple regression analysis, the following equation is the model fit for prediction of the experimental results:

$$\text{Yield (\%)} = 15.820 + 3.189X_1 + 0.778X_2 + 12.689X_3 - 0.645X_1.X_3 \quad (2)$$

The appropriateness of the prediction with the actual results are represented by plot in Figure 8. The predicted responses were in good agreement with the experimentally obtained

Table 6. The yield values at the varied condition.

Run	Time (X_1)	Methanol to RBO ratio (X_2)	Catalyst (X_3)	Yield (%)
1	20	5.5	3	86.60
2	10	5.5	2	70.30
3	30	8.0	3	99.90
4	30	5.5	4	98.00
5	10	3.0	3	76.80
6	10	5.5	4	99.20
7	20	3.0	4	98.33
8	20	5.5	3	88.90
9	20	5.5	3	87.90
10	20	3.0	2	85.59
11	20	8.0	4	97.20
12	10	8.0	3	96.70
13	30	3.0	3	98.00
14	30	5.5	2	94.90
15	20	8.0	2	94.80

Table 7. ANOVA results for full-factor analysis.

Source	DF	Sum of Square	Mean Square	*F*-value	*P*	
Regression	9	1025.29	113.922	9.21	0.012	Significant
Linear	3	674.98	224.993	18.19	0.004	Significant
X_1	1	285.61	285.605	23.09	0.005	Significant
X_2	1	111.60	111.602	2.54	0.030	Significant
X_3	1	277.77	277.77	9.02	0.005	Significant
Square	3	76.18	76.18	22.46	0.225	Not significant
X_1*X_1	1	0.58	2.57	2.57	0.667	Not significant
X_2*X_2	1	61.34	65.60	65.69	0.070	Not significant
X_3*X_3	1	14.26	14.26	14.257	0.332	Not significant
Interaction	3	274.14	91.380	7.39	0.028	Significant
X_1*X_2	1	81.00	81.00	6.55	0.051	Not significant
X_1*X_3	1	166.41	166.410	13.45	0.014	Significant
X_2*X_3	1	26.73	26.729	2.16	0.202	Not significant
Residual Error	5	61.85	12.369			
Lack-of-Fit	3	59.19	19.729	14.83	0.064	Not significant
Pure Error	2	2.66	1.33			
Total	14	1087.14				

response (R^2 = 0.989 and Adj R^2 = 0.977). Furthermore, the model's P-value of 0.00 implies that the model is significant.

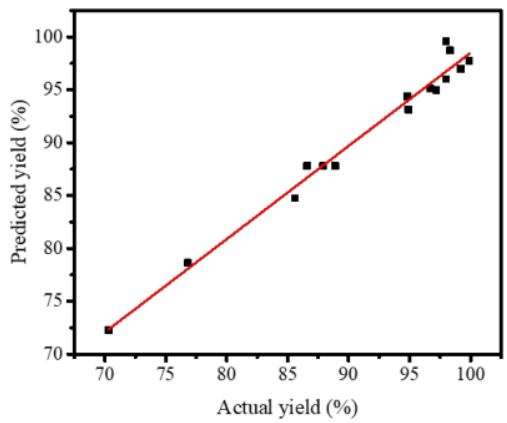


Figure 8. The appropriateness of the prediction with the actual results.

In more detail, the factors of time of reaction, methanol to oil ratio, and catalyst amount are significantly influence the yield. The surface plot in Figure 9(a) demonstrate that the higher yield obtained at the higher time of reaction, but then it is not significantly different at the catalyst dose of 3 and 4 g/100 mL. In addition, from the contour plot in Figure 9(b), in the perspective of time and methanol to oil ratio, the yield increases as both factors increased. It implies that the excess methanol tends to reach equilibrium for the transesterification reaction. However, the catalyst amount has an optimum condition as the surface interaction equilibrium was also influenced by the maximum capacity of the surface.

3.3 Catalyst Reusability

As the main factor to be considered in application scale, catalyst reusability is an important character. Figure 10(a) demonstrated

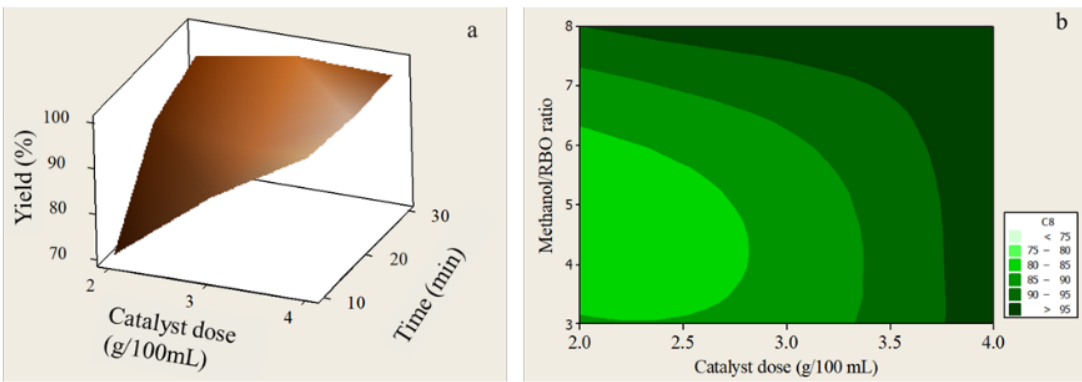


Figure 9. (a) Surface plot of the effect of catalyst dose and time of reaction to the yield, (b) Contour plot of catalyst dose and methanol/RBO ratio on to the yield.

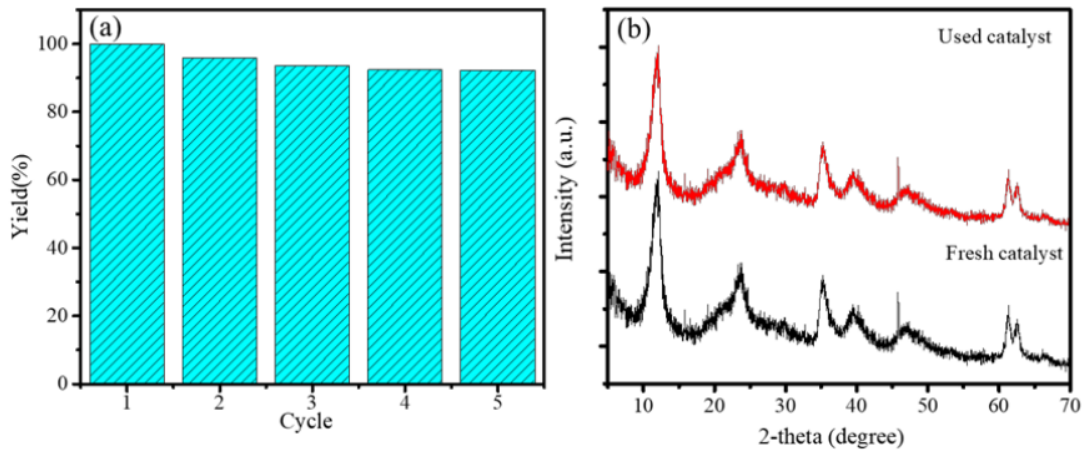


Figure 10. (a) Yield of biodiesel at varied cycle of reaction (b). XRD pattern of fresh and used KF/LDH catalyst.

the change of yield on reaction until 5th cycles. The recycling of the catalyst was conducted by washing in ethanol and water and dried at 100 °C. As shown from the bar chart that there is no significant change of the yield until 5th cycle. To confirm the effect of LDH structure, XRD analysis was conducted and give the patterns as shown in Figure 10(b). As there is insignificant change on the LDH structure, the activity loss is possibly caused by the reduced basicity cause of the blocking.

4. Conclusions

The results of the present studies show that KF modification onto Mg/Al-LDH was successfully prepared for enhancing catalytic activity in biodiesel production. Physicochemical characterization of materials revealed the increasing specific surface area of LDH as consequence of the KF impregnation, which identified by the appreciable amount of fluor element in SEM-EDX analysis and TEM analysis. The use of the response surface methodology-which is based on the Box-Behnken design-was applied for the optimization of catalyst dose, methanol-to-oil ratio, and the time of reaction the parameters. It can be concluded that all tested parameters strongly influence the yield of reaction. The KF/LDH catalyst is recyclable as it gave insignificant change of yield until 5th cycle of use, suggests that the material is potentially developed for biodiesel conversion.

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