

## Research Article

# Synthesis of Carbide Lime Waste Derived Base Catalyst (KF/CLW-Fe<sub>3</sub>O<sub>4</sub>) for Methyl Ester Production: An Optimization Study

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## Abstract

In this paper, solid base catalyst KF/CLW-Fe<sub>3</sub>O<sub>4</sub> was prepared from carbide lime waste, primarily calcium hydroxide with tiny amounts of carbonate and; the catalyst was used in the optimization study on the methyl ester production. The new strong base catalyst was synthesized by chemical impregnation. This catalyst was characterized by Hammett indicator analysis, Brunauer-Emmett-Teller (BET), scanning electron microscope (SEM), X-ray diffraction (XRD), and temperature-programmed desorption (TPD) of carbon dioxide. The catalyst was further used to catalyzed the transesterification reaction to produce methyl ester. Taguchi method was used to assess the impact of catalyst at different intervals of reaction parameters, including reaction time, methanol to oil ratio, and catalyst loading. A mixed level of orthogonal array design with L9, analysis of variance (ANOVA) and signal to noise ratio were used to determine parameters that significantly impact the palm oil transesterification reaction. High methyl ester conversion was attained, and the catalyst can be easily separated and reused. KF/CLW-Fe<sub>3</sub>O<sub>4</sub> has great potential to be used to produce methyl ester because of its high catalytic activity and environmental friendliness.

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**Keywords:** Solid base catalyst; carbide lime; transesterification; optimization; KF/CLW-Fe<sub>3</sub>O<sub>4</sub>

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## 1. Introduction

In this modern era, the world's energy demand is steadily increased due to industrialization, modernization, and development. The total

world energy consumption is estimated to be raised by 33.5% from 2010 to 2030 [1]. More petroleum-based products, such as fuel, are required to fulfil the high energy demand. As a result, this may cause non-renewable sources such as natural gas, petroleum, and coal to be running out soon. Next, it will raise the price of

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crude oil and have an impact on global economic activity [2]. Due to the adverse environmental effects of fossil fuels, such as global warming and climate change, widespread global concern for alternative energy has arisen. These are the serious issues that may endanger all living things on the planet. As a result of these challenges, researchers and scientists have been pushed to develop liquid biofuels as an alternative fuel. Biofuels are liquid fuels that can be produced from the plants and wastes, such as agricultural products. Biofuel production is constantly being researched and developed to increase its long-term viability and reliability as a supplementary energy source.

Biodiesel is considered one of the biofuels. It is a biodegradable and renewable fuel whose properties must meet ASTM and EN standards [3]. It can be used on its own or blended with petroleum-based diesel fuel at ratios that are suitable for conventional engines, such as the B20 blend [4]. Biodiesel can be produced by the transesterification method. This method involves converting triglyceride from vegetable oil or animal oil to methyl esters (with methanol) and the presence of a catalyst. Glycerol will also be formed during this process.

Homogeneous base catalysts, like potassium hydroxide (KOH) and sodium hydroxide (NaOH) are frequently utilized for methyl ester production. These catalysts are widely used in industries because of several advantages. Only a low reaction temperature and pressure are required; high conversion can be done in a short time, is readily available, and is cost-effective [5]. Although these catalysts are highly effective for the transesterification reaction, there are some disadvantages of this type of catalyst: incapable of catalyst reuse, hard to separate from the product, generate wastewater, and more [6–8]. Consequently, research into the development of heterogeneous catalysts has accelerated. Industrial and environmental waste materials can aid in the development of a cost-effective solid base catalyst. A sustainable and environmentally friendly approach toward methyl ester production can be promoted by exploring waste materials for the development of catalysts [9].

Malaysia is enriched with limestone resources. One of its uses is to produce acetylene gas. During the generation of acetylene gas, calcium hydroxide,  $\text{Ca}(\text{OH})_2$  will also be created, known as carbide lime. Carbide lime is designated as a scheduled waste since it is considered industrial waste in Malaysia [10]. The waste contains 85–95% calcium hydroxide, 1–10% calcium carbonate, and 1–3% silicates

[11,12]. This paper aims to study the optimization of methyl ester production by using the strong base catalyst (KF/CLW- $\text{Fe}_3\text{O}_4$ ) prepared from the carbide lime waste. There are very few reports on the utilization of carbide lime waste as the strong base catalyst for biodiesel production. However, carbide lime was used in the building material, water treatment and acid mine drainage treatment [13–15]. Without proper waste management, it will cause a severe negative impact on the environment. Therefore, proper utilization of the carbide lime waste can help reduce the potential negative cause of the waste. In order to investigate the effects of control factors and optimize the experimental conditions, the Taguchi Method was used as the experimental design methodology. The effect of reaction time, catalyst loading, and methanol/oil ratio on biodiesel production was examined.

## 2. Materials and Methods

### 2.1 Materials

The Mineral Research Centre, Rock Based Technology Section supplied carbide lime, 99% iron(II) sulfate hydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), 99.5% iron(III) sulfate hydrate ( $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$ ), ammonia solution, methanol, potassium fluoride, neutral red, bromothymol blue, phenolphthalein, nile blue, 99% 2,4 dinitroaniline, 4-nitroaniline and diphenylamine were purchased from Evergreen Engineering & Resources. The palm oil was purchased from the local market.

### 2.2 Preparation of KF/CLW- $\text{Fe}_3\text{O}_4$ Catalyst

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$  were dissolved in the distilled water with a ratio of 1:2. Then, Ammonia at a concentration of 20% was poured into the solution. The solution was left aging for 1 h. Black precipitation was formed, and  $\text{SO}_4^{2-}$  was removed by washing many times with distilled water. The KF/CLW- $\text{Fe}_3\text{O}_4$  catalyst was produced by using the calcination and impregnation method. The calcination of 50 g carbide lime was carried out at 850 °C for 4 h. The  $\text{Fe}_3\text{O}_4$  (5.0 g) and calcined product (20.0 g) combination was immersed in 25 wt% potassium fluoride and agitated for 1 h. After that, the mixture was dried in the oven at 105 °C for 24 h. The sample was calcined for 3 hours at 600 °C.

### 2.3 Characterization of Catalyst

Hammett Indicator was used to analyze the base strength of the catalyst. The Hammett In-

indicator testing method used neutral red, bromothymol blue, phenolphthalein, nile blue, 2,4 dinitroaniline, 4-nitroaniline, and diphenylamine as indicators. The temperature-programmed desorption of carbon dioxide (TPD-CO<sub>2</sub>) using TPDRO 1100 Series was carried out at Universiti Putra Malaysia to assess the catalyst's basicity. TPD-CO<sub>2</sub> was carried out with the use of a thermal conductivity detector (TCD) at temperatures ranging from 100 °C to 900 °C under helium flow. Cu K<sub>α</sub> radiation was emitted at a tube voltage of 40 kV, a current of 40 mA, and a scanning range of 10° to 90° for the XRD analysis using X'pert Pro. Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX) were used to study the morphology of the samples. The Brunauer–Emmett–Teller analysis (BET) was used to determine sample surface areas (Micromeritics ASAP2020).

#### 2.4 Transesterification Reaction

The transesterification reaction was performed in a 250 mL 3-neck flask on the hot plate equipped with thermocouple probe, condenser, and magnetic stirrer with a temperature of 60 °C and speed of 300 rpm. The catalyst was separated using a centrifuge after the reaction, and excess methanol was evaporated by heating the methyl ester produced at 70 °C. Biodiesel and glycerol were separated from the transesterified product.

#### 2.5 Optimization Study (Taguchi Method)

A Taguchi L9 (33) orthogonal array was used to investigate the factors influencing tri-

glyceride to FAME conversion. The effects of reaction time (60, 120, 180 min), methanol/oil molar ratio (5, 10, 15), and catalyst loading was studied (3, 6, 9 wt%). Gas chromatography (Model name: Agilent 7890A GC) was used to examine the methyl ester yield. FTIR analysis via Shimadzu IR Prestige-21 was carried out to recognize the functional group of the biodiesel. The yield of FAME can be determined by the following equation:

$$\%FAME = \frac{\sum A - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100\% \quad (1)$$

where,  $\Sigma A$  is total peak area from the FAME,  $A_{EI}$  is the peak area of methyl heptadecanoate,  $C_{EI}$  means concentration, in mg/mL of the methyl heptadecanoate solution,  $V_{EI}$  is the volume in mL of the methyl heptadecanoate solution and  $m$  is the mass in mg of the sample.

### 3. Results and Discussion

#### 3.1 Basic Strength Analysis

The Hammett Indicator was used to identify the base strength of the KF/CLW-Fe<sub>3</sub>O<sub>4</sub> catalyst. The catalyst's base strength was H = 22.5. The catalyst's basicity was further investigated using TPD-CO<sub>2</sub> method. The number of basic sites was calculated by using the integral method based on the area of the corresponding peaks [16]. The TPD-CO<sub>2</sub> profile of the KF/CLW-Fe<sub>3</sub>O<sub>4</sub> is shown in Figure 1. The low-temperature range (0–180 °C) could be attributed as weak basic sites, whereas the intermediate temperature range (180–400 °C) accounts for moderate basic sites, and the high-temperature range (>400 °C) contains data for

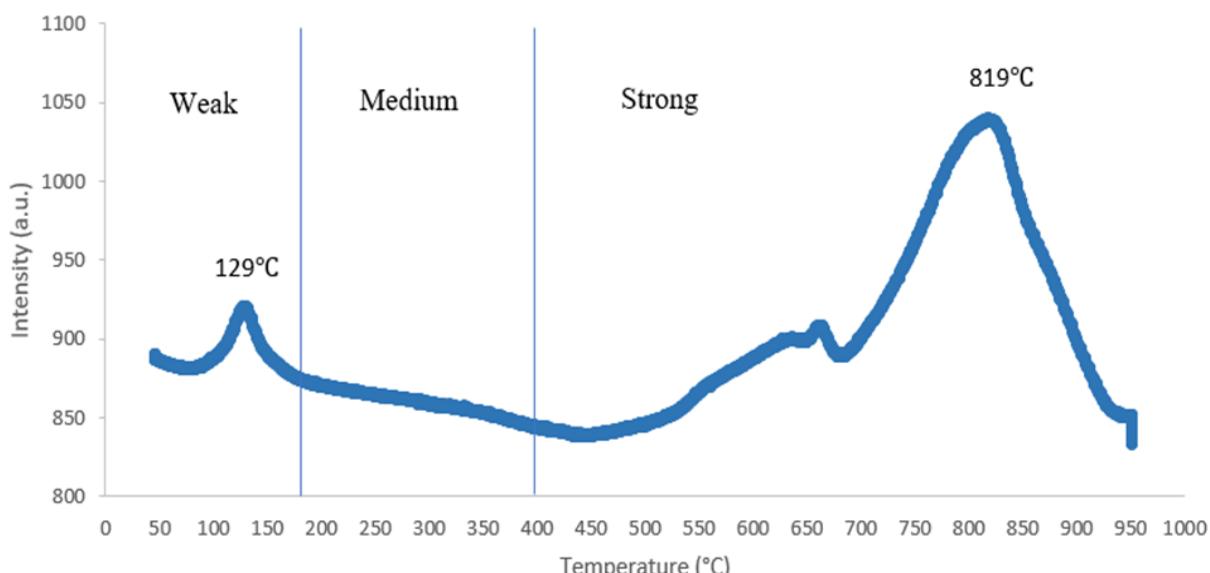


Figure 1. TPD-CO<sub>2</sub> profile of the KF/CLW-Fe<sub>3</sub>O<sub>4</sub> catalyst.

strong basic sites [17]. The overall amount of  $\text{CO}_2$  desorbed, and the amount of  $\text{CO}_2$  desorbed in each range is shown in Table 1. The catalyst's TPD- $\text{CO}_2$  result was in good agreement with the Hammett Indicator result. Catalysts with strong basicity can produce higher biodiesel yields with faster transesterification [18].

### 3.2 Morphology Analysis

Figure 2 displays the SEM images for carbide lime (1000x) and KF/CLW- $\text{Fe}_3\text{O}_4$  catalyst (1000x). Based on Figure 2 (a), the carbide lime waste had an uneven and irregular surface.

After calcination and impregnation, the KF/CLW- $\text{Fe}_3\text{O}_4$  catalyst particles agglomerated and formed into a large crystal structure. It can be seen that the catalyst is composed of small spherical grains.

### 3.3 BET Analysis

The BET surface area of carbide lime waste was  $56.31 \text{ m}^2/\text{g}$ , while for KF/CLW- $\text{Fe}_3\text{O}_4$  catalyst was  $1.77 \text{ m}^2/\text{g}$ . Due to impregnation, the KF/CLW- $\text{Fe}_3\text{O}_4$  catalyst's surface area was drastically reduced compared to carbide lime waste [19].

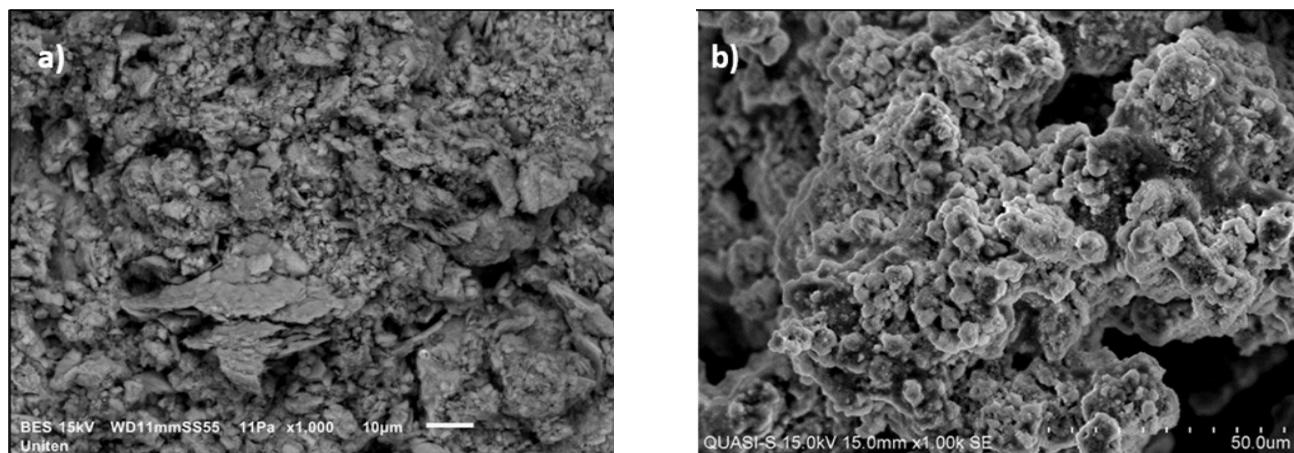


Figure 2. The SEM image of the (a) carbide lime waste (b) KF/CLW- $\text{Fe}_3\text{O}_4$  catalyst.

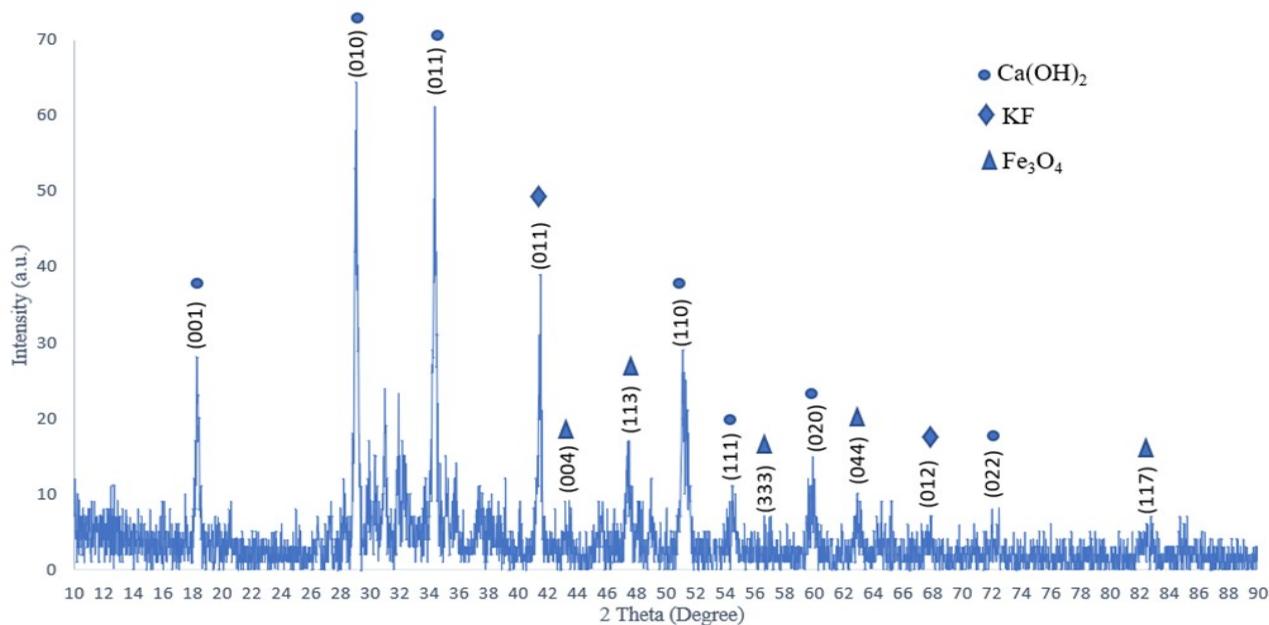


Figure 3. XRD result for KF/CLW- $\text{Fe}_3\text{O}_4$  catalyst.

Table 1. Amounts of  $\text{CO}_2$  desorbed in the  $\text{CO}_2$ -TPD experiments.

Sample	Weak (90–180 °C) ( $\mu\text{mol/g}$ )	Strong (>400 °C) ( $\mu\text{mol/g}$ )
KF/CLW- $\text{Fe}_3\text{O}_4$	128.91	2112.61

### 3.4 Structural Analysis

The XRD results of the KF/CLW- $\text{Fe}_3\text{O}_4$  catalyst are shown in Figure 3. Based on ICSD 98-005-8826, the XRD pattern for KF/CLW- $\text{Fe}_3\text{O}_4$  catalyst shows that  $\text{Ca}(\text{OH})_2$  was the dominating compound with diffraction peaks (001), (010), (011), (110), (111), (020), and (022). The  $\text{Fe}_3\text{O}_4$  of cubic structure is identified in the diffraction peaks (004), (113), (333), (044), and (117) (ICSD 98-011-1045). Then, the existence of KF with cubic structure is confirmed in the diffraction peaks (011) and (012) (ICSD 98-001-9261). Based on previous studies, the homogeneous distribution of magnetite substances on

the outer surfaces of the calcined CLW produce larger surface area and increase the basicity of the  $\text{Fe}_3\text{O}_4$ /CLW catalyst which improves the catalytic activity [20]. Furthermore, the basic strength and basicity of the catalyst was improved by adding KF onto the  $\text{Fe}_3\text{O}_4$ /CLW catalyst, which enhanced the performance of the catalyst for the transesterification [21].

### 3.5 Analysis of S/N

The yield of the methyl ester produced according to the designed nine sets of OA of experiments at different methanol/oil molar ratio (5, 10, 15), time (60 to 180 min), and catalyst loading (3, 6, 9 wt%) are shown in Table 2. MINITAB-14 was used for the analysis of these results. Table 2 shows that the highest methyl ester yield (81.04%) was attained at the reaction time of 60 min, methanol to oil ratio of 10:1, and catalyst loading of 6 wt%.

Taguchi proposes using the S/N ratio to assess quality characteristics that deviate from desired values. For the S/N ratio analysis, there are three types of quality characteristics: "smaller the better," "larger the better," and "nominal the better" [22]. A higher S/N ratio indicates higher quality characteristics regardless of the type of quality characteristics. Consequently, level of process parameters with the highest S/N ratio is the optimal level. The S/N ratio of the experiments is shown in Table 3 and represented graphically in Figure 4.

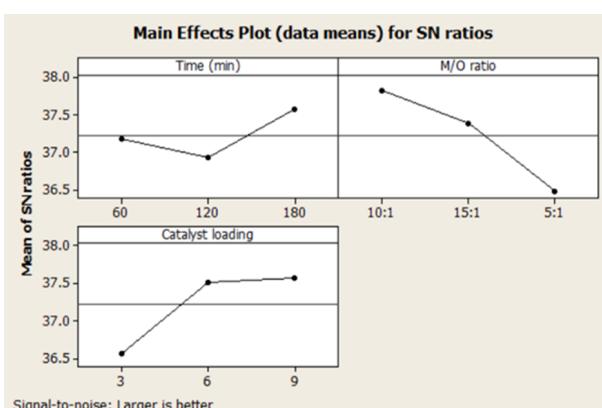


Figure 4. Mean effects plot for "Larger is Better" S/N ratio analysis for production of methyl ester by KF/CLW- $\text{Fe}_3\text{O}_4$  catalyst at different time intervals, M/O molar ratio, and catalyst loading.

Table 2. Experimental results of the methyl ester produced by KF/CLW- $\text{Fe}_3\text{O}_4$  catalyst at different intervals, methanol/oil ratio, catalyst loading.

Time (min)	Methanol to oil ratio	Catalyst loading (wt%)	FAME Yield (1) (%)	FAME Yield (2) (%)	Averaged FAME Yield (%)
60	5:1	3	57.78	62.58	60.18
60	10:1	6	81.53	80.55	81.04
60	15:1	9	78.19	76.02	77.11
120	5:1	6	67.38	66.79	67.09
120	10:1	9	74.41	78.91	76.66
120	15:1	3	75.99	58.44	67.22
180	5:1	9	72.91	73.41	73.16
180	10:1	3	69.68	81.53	75.61
180	15:1	6	74.66	81.18	77.92

Table 3. Response table for S/N ratio at different time intervals, M/O ratio, and catalyst loading.

Level	Time (min)	M/O ratio	Catalyst loading (wt%)
1	37.17	37.81	36.57
2	36.92	37.38	37.51
3	37.56	36.47	37.57
Delta	0.64	1.34	1.00
Rank	3	1	2

Figure 4 shows that the methanol to oil molar ratio has a high value of SN ratio, followed by catalyst loading and reaction time. The methyl ester production increased with the increasing methanol to oil molar ratio until it reached the optimum condition, which is 10:1; the methyl ester yield decreased if the methanol to oil molar ratio was higher than 10:1. This drop may be due to an excess of methanol, which increases glycerol solubility and interferes with the separation of alkyl ester and glycerol. As a result, foam formation caused a noticeable loss of ester product due to a portion of the remaining diluted glycerol in the alkyl ester process [23]. Furthermore, the yield of the methyl ester increased as the catalyst loading increased. The findings suggest that increasing catalyst loading will increase the catalyst's active surface area in the transesterification reaction, thereby increasing methyl ester yield [24]. The results also show that 180 min is the best reaction time for methyl ester production using KF/CLW-Fe<sub>3</sub>O<sub>4</sub> catalyst. The yield of methyl es-

ter produced at this reaction time is similar even though the catalyst loading and M/O molar ratio differ. Due to the reactants initially form a two-phase liquid system, methyl ester yield drops from 60 min to 120 min of reaction time due to an unstable reaction and the difficulty of mixing and dispersing alcohol into the oil [25]. The results calculated that optimum parameters are reaction time of 180 min, M/O molar ratio of 10:1, and catalyst loading of 9 wt%.

### 3.6 ANOVA Results

ANOVA examines the variance in the results induced by each parameter in relation to the overall variation. Standard terms in an ANOVA table, such as sum of squares (SS), variance (V), F-values (F), and percent contribution (PC), are calculated [22]. If the F-value is 6.3589 (99% of confidence level), a parameter significantly impacts the response; if F-value is 3.6824, it has a significant influence (95% of confidence level). It does not mean that if a parameter's F-value is less than 3.6824, the parameter has no impact on the response. It simply means that the difference in the response caused by changes in the parameter's levels is negligible in comparison to the errors in the range of the selected levels [22]. The P-

Table 4. ANOVA results for methyl ester production at different time intervals.

Source	DF	SS	MS	F	P
Time (min)	2	41.2	20.6	0.39	0.693
Error	6	317.3	52.9		
Total	8	358.5			

Table 5. ANOVA results for methyl ester production at different M/O ratio.

Source	DF	SS	MS	F	P
M/O Ratio	2	186.6	93.3	3.26	0.110
Error	6	171.9	28.7		
Total	8	358.5			

Table 6. ANOVA results for methyl ester production at different catalyst loading.

Source	DF	SS	MS	F	P
Catalyst Loading	2	122.6	61.3	1.56	0.285
Error	6	235.9	39.3		
Total	8	358.5			

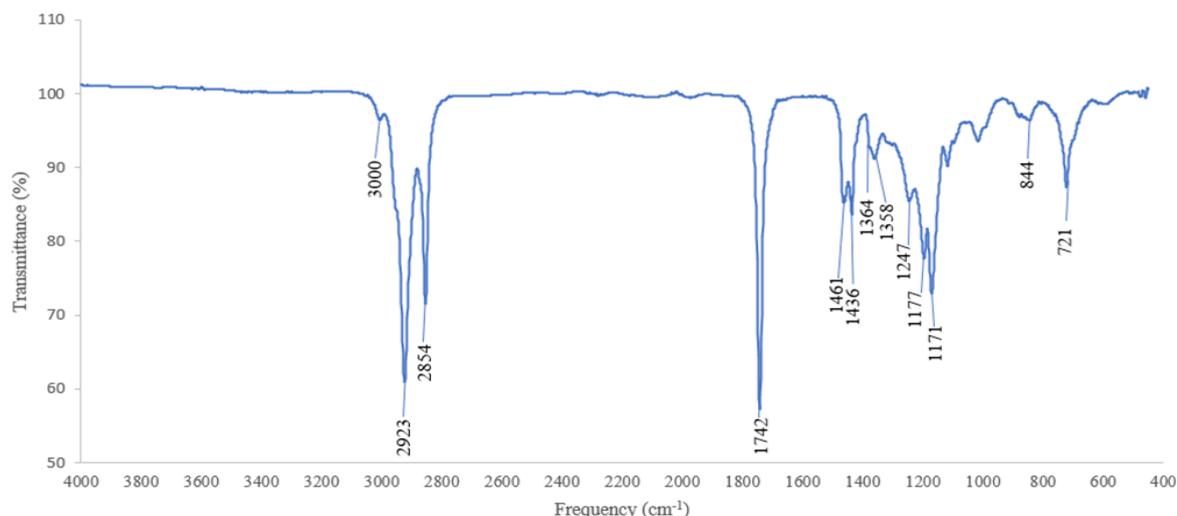


Figure 5. FT-IR spectra of methyl ester produced at the time interval of 60 min, catalyst loading of 6 wt%, and M/O molar ratio of 10:1 by KF/CLW-Fe<sub>3</sub>O<sub>4</sub> catalyst.

values are a method to identify each variable's significance and show the relationship between each independent variable. The smaller the p-values, the higher the significance of the corresponding variables. If the P-values less than 0.05, it means that the variable is significant. Table 4 to Table 6 shows that the M/O molar ratio has the smallest P compared with the other two-parameter; it is the most significant parameter on methyl ester production, followed by the catalyst loading.

### 3.7 Determination of Ester Group

The functional group for the esters in biodiesel was investigated using FT-IR analysis. Table 2 shows that the yield of methyl ester produced at the time interval of 60 min, catalyst loading of 6 wt%, and M/O molar ratio of 10:1 is the highest; the methyl ester had been used for the FT-IR analysis. Figure 5 indicates the FT-IR spectra of methyl ester produced at the time interval of 60 min, catalyst loading of 6 wt%, and M/O molar ratio of 10:1 by KF/CLW- $\text{Fe}_3\text{O}_4$  catalyst. According to the literature review, FT-IR spectra of produced biodiesel are remarkably comparable to palm oil [26,27]. Frequencies of  $1742\text{ cm}^{-1}$  in Figure 5 indicate that the biodiesel contains the C=O stretch ester bond. The C–O stretch bond can be seen at frequencies  $1171\text{ cm}^{-1}$ ,  $1177\text{ cm}^{-1}$ , and  $1247\text{ cm}^{-1}$ . These peaks are comparable to those found in palm oil. The peak at  $1461\text{ cm}^{-1}$  specifies the methyl ester group that results from transesterification [26]. Due to the presence of these ester groups, the palm oil was proven converted successfully into methyl ester utilizing KF/CLW- $\text{Fe}_3\text{O}_4$  as the catalyst.

## 4. Conclusions

In conclusion, KF/CLW- $\text{Fe}_3\text{O}_4$  catalyst exhibits outstanding catalytic performance in the transesterification reaction. 81.04% of methyl ester yield was achieved at the reaction time of 60 min, M/O molar ratio of 10:1, and catalyst loading of 6 wt%. The optimization study indicates that the M/O molar ratio is the most significant parameter followed by catalyst loading and reaction time for methyl ester production. The optimum parameters calculated from this work are reaction time of 180 min, M/O molar ratio of 10:1, and catalyst loading of 9 wt%. This work shows the new potential for the utilization of waste resources. The KF/CLW- $\text{Fe}_3\text{O}_4$  catalyst's strong basicity reveals that it has promising uses in the biodiesel sector and contributes to a waste-free environment.

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