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Research Article

Cu^{2+} Montmorillonite K10 Clay Catalyst as a Green Catalyst for Production of Stearic Acid Methyl Ester: Optimization Using Response Surface Methodology (RSM)

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Abstract

Clay catalyst has received much attention to replace the homogeneous catalysts in the esterification reaction to produce fatty acid methyl ester as the source of biodiesel as it is low cost, easily available, as well as environmental friendly. However, the use of unmodified clay, in particular montmorillonite K10 (MMT K10), for the esterification of fatty acids showed that the acid conversion was less than 60% and this is not preferable to the production of biodiesel. In this study, synthesis of stearic acid methyl ester using Cu^{2+}-MMT K10 (Cu-MMT K10) was successfully optimized via response surface methodology (RSM) based on 3-variable of Box-Behnken design (BB). The parameters were; reaction time (5-180 minutes), reaction temperature (80-120 °C) and concentration of Cu^{2+} in MMT K10 (0.25-1 M). The use of RSM in optimizing the conversion of stearic acid was successfully developed as the actual experimental conversion of stearic acid was found similar to the actual values under the optimum conditions. The model equation predicted that the following conditions would generate the maximum conversion of stearic acid (87.05 % reaction time of 62 minutes, a reaction temperature of 80 °C and catalyst used is 1.0 M Cu-MMT K10. This finding can be considered as green catalytic process as it worked at moderate reaction temperature using low cost clay catalyst with a short reaction time. Copyright © 2018 BCREC Group. All rights reserved

Keywords: Montmorillonite K10; esterification; response surface methodology; stearic acid methyl ester

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1. Introduction

Esterification of fatty acids is very important as this can contribute to the production of biodiesel. Biodiesel, derived from renewable oils or fats, is alkyl esters of long-chain fatty acid, has become the focus of international attention as a source of energy. This is due to the fact that it is environmentally friendly, non-toxic, biodegradable, reduces the emission of carbon dioxide in the atmosphere and emits pollutants less than

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normal diesel [1-2]. The esterification reaction normally carried out using homogeneous catalysts such as sulfuric acid, but using such catalyst has some difficulties such as the corrosion of equipment, waste generation and environmental problems [3]. The emphasis on environmental protection, as industrial and economic growth gave birth to many forms of pollution threatening human health and earth ecosystems, resulted in the growth of environmental catalysis.

Recently, focus has been centered on the use of clay minerals as heterogeneous catalysts due to their properties; low cost, easily available, as well as environmental friendly [4]. Montmorillonite K10 (MMT K10), the major clay mineral commercially available has been used as a heterogeneous catalyst for many applications [5], [6]. There are considerable methods which can be used to modify MMT to improve its catalytic properties, such of these methods include cation exchanged. This method is considered as an efficient method as it produces the catalyst that is reusable without losing its catalytic activity, also increasing the strength of Brønsted and Lewis acid site [7]. Cation-exchanged MMT clays (Al^{3+}, Fe^{3+}, Cr^{3+}, Zn^{2+}, Cu^{2+}, and Ni^{2+}) have been used as catalysts in esterification of succinic acid with iso-butanol, with conversion higher than 90% after 8 hours of reaction [8].

Optimization of reaction process is very important to improve the reaction performance. Optimization study by changing one parameter at a time may involve a larger number of experiments to be studied and difficult to be understood since more than one variable can simultaneously influence the system. Thus, statistical approach, such as response surface methodology (RSM), is normally used as this method able to give the relationship between the best conditions of the factors to optimize a desired product. The RSM is a useful statistical technique for optimization of complex processes, as it reduces the number of experiments required to achieve ample data for a statistically pertinent result [9-10]. The RSM has been applied in the optimization of biodiesel synthesis from esterification of free fatty acid using solid material such as PA/NaY (PA = organophosphonic acid) [11], organophosphonic acid-functionalized silica [12], and sulfonated cation exchange resins [13].

This work focuses on the use of Cu^{2+}-exchanged MMT K10 as catalyst for esterification of stearic acid as to date there is no work has been done on this catalyst for esterification of long chain acid. Our group has reported on the application of Fe^{3+}-exchanged MMT K10 as heterogeneous acid catalyst for the production of stearic acid esters [14]. The purpose of this work is to study the optimization process of methyl stearate synthesis using Cu^{2+} modified MMT K10. A series of Cu-MMT K10 were prepared from the Cu ion solutions and MMT K10 by cation exchange method and their structures were studied by x-ray diffraction (XRD) and the elemental analysis was done by energy-dispersive x-ray spectroscopy (EDX). The optimization process of methyl stearate synthesis was conducted using statistical approach of RSM by investigating three reaction parameters i.e. reaction time, reaction temperature and concentration of Cu^{2+} ion in the modified MMT K10.

2. Materials and Methods

2.1 Preparation and characterization of Cu-MMT K10

A series of Cu-MMT K10 catalysts were prepared by adding 10 g of MMT K10 (Acros Organics) to 100 mL aqueous solution of $Cu(COOCH_3)_2.H_2O$ (R & M Chemicals) under stirring at various concentrations, i.e. 0.25, 0.5, 0.7, and 1 M at 80 ^oC for 8 hours. Then the slurry was cooled, filtered and washed thoroughly with distilled water. The samples were dried at room temperature, then at 100 °C for 12 hours, followed by calcination at 300 °C for 4 hours [15]. The crystalline phases of Cu-MMT K10 catalysts were characterized by XRD. The XRD analysis was performed through Cu Kα radiation. The data in intensity was plotted in a chart based on 2θ in a range of 5^o-60^o. Energy-dispersive X-ray spectroscopy analysis (EDX) (Horiba EMAX model EX 250) was carried out to determine the amount of Cu in the MMT K10. The distribution of Brønsted and Lewis acid sites on the surface was measured using the pyridine adsorption followed by the FTIR analysis. The solid catalyst ca. 0.5 g was dried in an oven for 1 hour at 100 ºC, then 0.1 cm^3 of pyridine was exposed to the samples overnight. The samples were re-dried at 120 ºC for one hour to remove the physisorbed pyridine. The Lewis and Brønsted acids were determined by FTIR using the KBr pellet. The FTIR analyses of the catalysts were carried out over the frequency range of 1650-1350 cm^{-1} using the Varian equipment model 3100.

2.2 Optimization of methyl stearate

The reaction system consisted of 2 g of the stearic acid and 100 mL of alcohol was mixed and heated up until it reached the reaction temperatures (80, 100, and 120 °C). The sample was taken at this time considering the initial concentration of acid (a_i). After that 600 mg of catalyst (unmodified and modified MMT K10 samples) was added into the reactor. The percentage of stearic acid conversion to ester was determined by titration with 0.02 M NaOH. The samples were taken from the reactor for every 5 minutes in the first hour, and every subsequent hour for 3 hours. The conversion of the stearic acid was calculated using the following formula (Equation (1)):

$$\text{Conversion (\%)} = X_{acid} = (a_i - a_t) / a_i \times 100 \qquad (1)$$

where (a_i) is the initial acidity of at t_0 and (a_t) is the acidity at (t) time.

2.3 Experimental design

The three factors of Box-Behnken design (BB) was employed. The matrix consisted of 18 experiments with 12 fact points and 6 centre points. The variables and their respective levels are presented in Table 1. The parameters were chosen based on the previous studies [11-13] as well as on the conventional optimization study using one parameter at a time approach. The regression analysis, statistical significance of the models (ANOVA) and response surface were performed using computer software of Design Expert Version 9.0.6.2 (Stat-Ease Inc., Statistic Made Ease, Minneapolis, MN, USA).

3. Result and discussion

3.1 X-Ray diffraction

XRD of unmodified and modified MMT K10 samples are shown in Figure 1. X-ray patterns reveal that Cu-MMT-K10 at all concentrations have structural characteristics nearly identical to the unmodified MMT K10. XRD patterns of all samples show that the peak at a 2θ of ~8.8°, which is related to the presence of 2:1 (T-O-T) structure with basal d(001) reflection. The remarkable similarities between the diffractograms of the samples indicate that clay structure is retained during the exchanged processes. The retained structure of clay refers to the interlayer clay was not affected by the modification process and it is consistent with what has been studied previously by Fang *et al.* [16] who suggested that the Cu^{2+} ions are fixed solely on the outer surface of the clay. A similar observation was also reported in the case of Zn^{2+} and Fe^{3+} exchanged montmorillonite clay [17]. Whereas, inclusion of metal cations would increase the d values [18,19].

Table 1. Independent variables and levels used for CCD

Symbols	Factors	Unit	Levels	
			-1	1
A	Reaction time	min	5	180
B	Cu^{2+} concentration	M	0.25	1
C	Temperature	°C	80	120

3.2 Energy-dispersive X-ray spectroscopy analysis (EDX)

From the EDX data (Table 2), the unmodified MMT K10 sample has five elements detected, i.e. oxygen (O), silicon (Si), iron (Fe), aluminium (Al), and magnesium (Mg). These elements represent the components of MMT K10. The oxygen which coordinated with Si^{4+} tetrahedrally and Al^{3+} octahedrally while the Mg^{2+} is the exchangeable cation located between the parallel clay layers and around the edges of the layers. It can be seen that the main elements in MMT K10 were O^{2-} and Si^{4+} for all samples in the range of ca. 62-67 % and ca. 17-26 %, respectively. The Cu content in the prepared samples is in accordance with varied Cu content in the exchange process where the higher concentration of Cu^{2+} solution content produced a higher Cu percentage in the modified MMT K10. The calculated ratio of exchangeable Mg^{2+} with Cu^{2+} content gave a sharp increase between 0.25 M and 1.0 M Cu-MMT K10. However, the exchangeable Mg^{2+} shows no significant differences between 0.25 M and 1.0 M Cu-MMT K10 samples and this could be due to the Cu^{2+} ions are located at the outer surface of the clay as observed in the XRD patterns mentioned earlier. The reduced amount of silica and alumina could probably due to some leaching during filtration and cal-

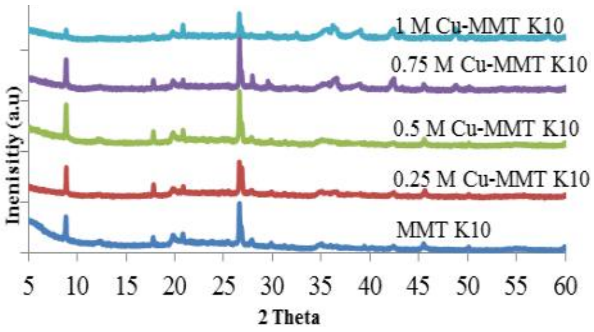

Figure 1. X-ray diffractograms for unmodified and Cu^{2+} modified MMT K10

cination processes [20]. Based on the previous works, it was revealed from the diffuse reflectance UV-vis spectrum that Cu exists as Cu^{2+} in MMT clay structure as Cu-MMT K10 exhibited a strong band with a maximum at 549 nm which is attributed to the *d-d* transitions of Cu(II). This band however was not appeared in MMT K10 sample [7,15].

3.3 Surface acidity

The effect of pyridine adsorption on the MMT K10 and Cu-MMT K10 surfaces can be observed from FTIR spectra shown in Figure 2. The unmodified MMT K10 showed a broad peak in the region of 1600-1700 cm^{-1} and a small peak at ca. 1490 cm^{-1} that can be assigned as the combination of Brønsted and Lewis acidities. These peaks became more intense as the Cu^{2+} content in MMT K10 structure increased. The appearance of a peak at ca. 1450 cm^{-1} is related to the Lewis acid site and this peak increased progressively from 0.25 M to 1 M MMT K10 samples indicating an increase in the strength of the Lewis acid site. These peaks assignments were done based on the previous works [7,8,17,18,21-23].

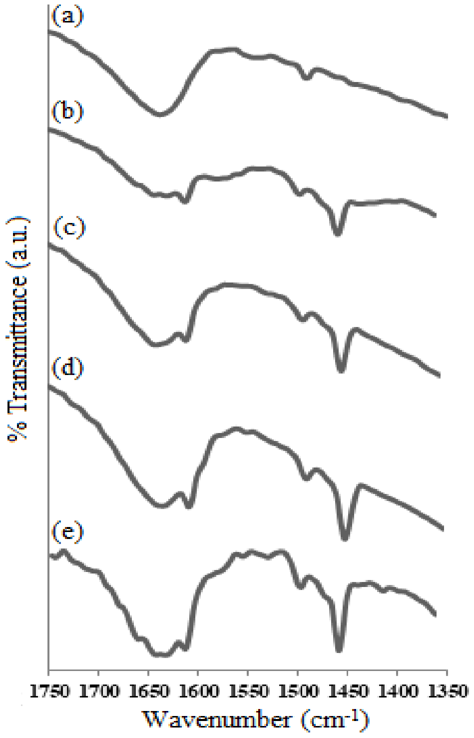

Figure 2. FTIR of pyridine adsorption on (a) unmodified MMT K10, (b) 0.25 M Cu-MMT K10, (c) 0.5 M Cu-MMT K10, (d) 0.75 M Cu-MMT K10 and (e) 1 M Cu-MMT K10

3.4 Model fitting and ANOVA

The relationship between response (stearic acid conversion) and three independent factors (reaction time, concentration of Cu^{2+} and reaction temperature) were analyzed. The results at each point are based on the experimental design and the actual values are shown in Table 3. The coefficients of the empirical model and their statistical analysis evaluated by ANOVA using Design Expert software are presented in Tables 4 and 5. The model was derived in terms of coded factors for stearic acid conversion is shown in Equation (2):

$$X = 55.24 + 3.71A + 6.31B - 8.08C + 2.47AB - 2.65AC - 6.38BC - 0.047A^2 + 11.28B^2 + 2.86C^2 \quad (2)$$

where positive and negative signs in front of the terms indicate synergistic and antagonistic effects, respectively.

The computed *F*-value of 31.50 for methyl stearate with *Prob* > *F*-value < 0.0001 implied that the model was significant at 95 % confidence level (*Prob* > *F* less than 0.0500). This high value of *F*-value indicates that the regression model is reliable in predicting the conversion of stearic acid to methyl stearate [24]. The low value of probability (P = 0.0001) and high coefficients of determination (R^2 = 0.9726) of the model indicates the suitability of the model for adequately representing the real relationship among the parameters studied. This R^2 value indicates that the sample variation of

Table 2. Elemental compositions (%) from EDX analysis of unmodified and Cu^{2+} modified MMT K10 (n.d. : not detected)

Sample	O	Si	Al	Mg	Fe	Cu
MMT K10	67.8±0.2	25.8±0.2	4.6±0.1	0.9±0.1	0.6±0.1	n.d
0.25 M Cu-MMT K10	67.2±1.1	23.3 ±0.5	4.9±0.9	0.6±0.05	0.6±0.1	3.4±0.1
0.5 M Cu-MMT K10	66.8±0.7	22.8±1.2	4.7±0.3	0.6±0.0	0.6±0.1	4.5±1.3
0.75 M Cu-MMT K10	64.9±0.2	21.5±0.5	4.5±0.3	0.6±0.0	0.6±0.1	7.9±0.7
1 M Cu-MMT K10	62.4±0.7	17.0±1.3	3.5±0.3	0.5±0.3	0.6±0.5	16.0±2.6

97.26% for stearic acid conversion is attributed to the independent variables and only 2.74% of the total variations are not explained by the model. The value of adjusted determination coefficient (Adj-R^2 = 0.9417) is also very high to support for a high significance of the model. High value of R^2 i.e. 0.98 has also been reported by Embong *et al*. [25] for methyl esters prepared from palm fatty acid distillate using SO_4^{2-}/TiO_2-SiO_2 as a solid acid catalyst and 0.9643 reported by Liu *et al*. [26] in the esterification of free fatty acid over solid phosphoric acid/NaY catalyst.

The result of coefficients estimate from the quadratic model (Table 5) showed positive values for the reaction time and concentration of Cu^{2+} in MMT K10. These factors had a significant effect in the conversion of stearic acid to

Table 3. Design matrix of the actual and predicted values of percentage of stearic acid conversion (*X*) in BB (*A*: Reaction time, *B*: Concentration of Cu^{2+}, *s*: Reaction Temperature)

Run	Factors			Actual Conversion (%)	Predicted Conversion (%)
	A (min)	B (M)	C (°C)		
1	5	0.25	100	59.98	58.91
2	180	0.25	100	64.79	61.4
3	5	1	100	63.21	66.6
4	180	1	100	77.9	78.97
5	5	0.625	80	60.79	59.75
6	180	0.625	80	71.21	72.49
7	5	0.625	120	50.2	48.91
8	180	0.625	120	50	51.03
9	92.5	0.25	80	62.66	64.76
10	92.5	1	80	92.5	90.14
11	92.5	0.25	120	59	61.35
12	92.5	1	120	63.34	61.23
13	92.5	0.625	100	55.24	55.24
14	92.5	0.625	100	55.24	55.24
15	92.5	0.625	100	55.24	55.24
16	92.5	0.625	100	55.24	55.24
17	92.5	0.625	100	55.24	55.24
18	92.5	0.625	100	55.24	55.24

Table 4. ANOVA for the regression model

Source	Sum of squares	Degrees of freedom	Mean of square	F-value	Prob > F
Model	1796.18	9	199.58	31.50	< 0.0001[a]
Residual	50.68	8	6.33		
Lack of fit	50.68	3	16.89		
Pure error	0.00	5	0.00		
Total	1846.85	17			
Std. Dev.	2.52				
Mean	61.50				
R-Squared	0.9726				
Adj R-Squared	0.9417				
Adeq Precision	21.978				

[a] Significance at Prob > F is < 0.050

methyl stearate. Meanwhile, the negative values of coefficients estimated a negative influence of the parameters on the reaction. The quadratic term of concentration of Cu^{2+} (B^2) is more significant than the quadratic term of reaction temperature (C^2) with high value of coefficient determination of $R^2 = 0.9726$ and low value of probability ($P = 0.0001$). The presence of Cu^{2+} in the clay structure has increased the Brønsted acidity of the clay. This is expected to give significant effect on the value of stearic acid conversion than the reaction time as esterification reaction is initiated by the protonation of carboxylic acid in presence of Brønsted acid catalyst [8].

3.5 Response surface plot

Equation (2) derived from regression analysis was then used to facilitate the plotting of response surface. Two parameters were plotted at one time on the X_1 and X_2 axes, respectively, with the other one remaining parameter set at its centre point values using 3D response surface, which represent the relationship between the responses and the parameters. Figure 3 (a) to (c) illustrate the response surface plots of interactive effect of reaction time (*A*), concentration of Cu^{2+} (*B*) and reaction temperature (*C*). Figure 3(a) shows the dependency of reaction time and Cu^{2+} concentration towards the conversion of stearic acid at a constant temperature (100 °C). The interaction between reaction time and Cu^{2+} concentration were significant to the stearic acid conversion and this optimization was also obtained using the conventional method. As can seen from the figure, the stearic acid conversion increased as reaction time increased from 5 to 110 min at any given Cu^{2+} concentration. However, prolonged the reaction time to 180 min gave no significant improvement on the conversion of stearic acid. At longer reaction time, the reaction would reached its equilibrium and thus no further conversion was observed [27]. Esterification is a reversible reaction and produces water as the by-product. Therefore, water generated will inhibit the forward reaction of stearic acid. As to compare, the esterification of free fatty acid in homogeneous catalyst (H_2SO_4) was achieved in

Table 5. Values of significant of regression coefficients

Factor	Coefficient Estimate	*Prob > F*
Intercept	55.24	< 0.0001[a]
A-Reaction Time	3.71	< 0.0031[a]
B-Concentration of Cu^{2+}	6.31	0.0001[a]
C-Reaction Temperature	8.08	< 0.0001[a]
AB	2.47	0.0853
AC	2.65	0.0679
BC	6.38	0.0010[a]
A^2	-0.047	0.9695
B^2	11.28	< 0.0001[a]
C^2	2.86	0.0451

[a]Significance at *Prob > F* is < 0.050

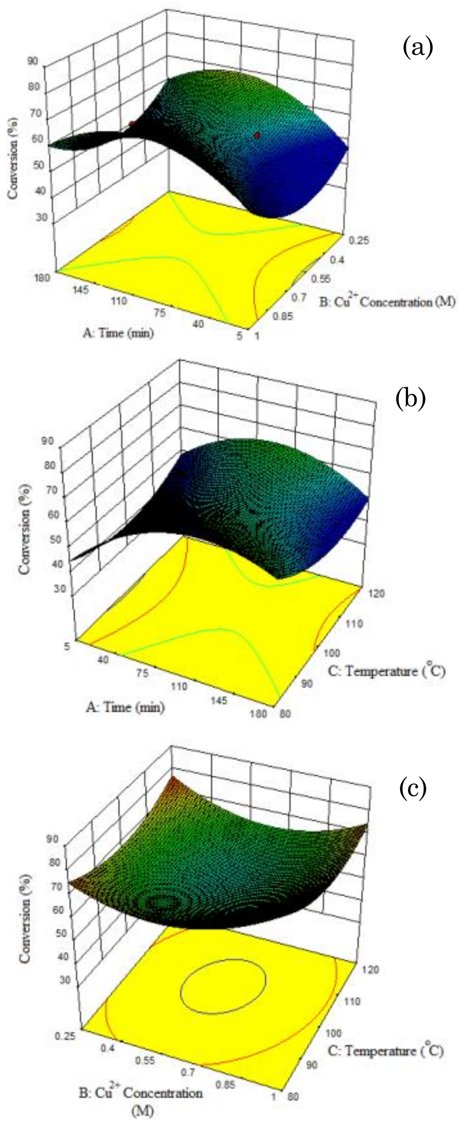

Figure 3. Response surface plot showing the effect of (a) reaction time versus catalyst concentration on the percentage conversion of stearic acid at fixed temperature 100 °C, (b) reaction time versus temperature on the percentage conversion of stearic acid at fixed catalyst concentration at 0.625 M, and (c) catalyst concentration versus temperature on the percentage conversion of stearic acid at fixed reaction time at 92.5 minutes

15 minutes [28]. However, esterification with H_2SO_4 suffers from several drawbacks, such as corrosive, the existence of side reactions and the fact that the catalyst cannot be easily separated from the reaction mixture.

The response surface indicates that for low temperatures, conversion of stearic acid increased with an increasing reaction time but reached its optimum at 110 min (Figure 3b). Maximum conversion is therefore obtained from optimum reaction time (110 min). This is due to the most significant factor being the reaction time therefore to its effect being positive value and temperature of reaction gave negative contribution to the conversion of stearic acid (see Table 5). As esterification reaction is a reversible reaction, increasing the reaction temperature resulted in the decrease of stearic acid conversion; and this could be due to loss of methanol at higher temperature [29]. Figure 3 (c) depicts the contributions of Cu^{2+} concentrations and temperature towards the conversion of stearic acid at constant reaction time (92.5 min). The 3D surface plot showed that higher conversion of stearic acid is strongly favored when high concentration of Cu^{2+} is employed at 80 ^{o}C. The Brønsted acid site of Cu-MMT K10 was found to improve as compared to the unmodified MMT K10. The increased concentration of Cu^{2+} has also improved the Brønsted acidity of the Cu-MMT K10 and thus increased the conversion of stearic acid. Brønsted acid sites act as the active sites that present in the interlamellar water molecules on the edge sites which coordinated to the exchangeable ions. This Brønsted acid sites then protonate the stearic acid and promote the esterification reaction with methanol [8].

3.6 Optimization condition

The optimum condition of synthesis of methyl stearate was predicted using the optimization function of the Design Expert Software. Empirical model derived from RSM discussed previously can be used accurately to describe the relationship between the factors and response in the conversion of stearic acid. Table 6 shows the optimum conditions with desirability 1 M concentration of Cu^{2+} in MMT K10 for stearic acid conversion generated from the model developed in Equation (2). Economically preferred to apply short reaction time (62 min) and relatively low reaction temperature (80 ^{o}C) for synthesis of methyl stearate from the reaction between stearic acid and methanol using 1.0 M Cu-MMT K10. This optimum condition can be used to produce high acid conversion up to ca. 87.05%. In the formation of n-butyl stearate using PA/NaY catalyst (PA=1-hydroxyethylidenediphosphonic acid) [29], the optimum conditions used to produce 87.67% conversion of stearic acid were 2 hours of the reaction time and 125 ^{o}C of the reaction temperature. While using organophosphonic acid-functionalized silica produced 78.14% ethyl oleate under optimum conditions of 112 ^{o}C for 10 hours [12]. From the obtained catalytic activity of 1 M Cu^{2+} modified MMT K10, it is possible to conclude that this catalyst is a promising solid acid catalyst for esterification of stearic acid as it performed at low reaction temperature and short reaction time.

Table 6. Predicted values of optimization conditions for strearic acid conversion generated from the model

A (min)	*B* (M)	*C* (^{o}C)	Predicted Conversion (%)
180	0.25	80.04	68.59
62	1	80	87.05
104.7	0.25	120	61.16
5	0.26	120	61.97
180	0.63	80.19	72.34

4. Conclusions

Comparison of predicted and experimental values of esters revealed a good correspondence between them, thus indicating the suitability of the models developed and the success of RSM in optimizing the conversion of stearic acid. The model derived from RSM can be used to adequate describe the relationship between factors and response in cation exchanged MMT K10 catalysed synthesis of methyl stearate. Prepared catalysts were able to give the high stearic acid conversion up to 87.05% in a short reaction time (62 min) at 80 ^{o}C. This obtained results together with the advantages hold by the MMT K10 clay such as present in abundance, low cost, as well as eco-friendly, and modification of clay only requires simple step open up the application of clay as catalyst for many of organic synthesis.

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