ASEAN Journal of Chemical Engineering 2023, Vol. 23, No. 1, 40 – 51

Box-Behnken Design for Optimization on Esterification of Free Fatty Acids in Waste Cooking Oil Using Modified Smectite Clay Catalyst

Achanai Buasri *
Suthita Lertnimit
Arnon Nisapruksachart
Issara Khunkha
Vorrada Loryuenyong
Department of Materials Science and Engineering, Faculty of Engineering and IndustriaTechnology, Silpakorn University, Nakhon Pathom, 73000, Thailand
*e-mail: achanai130@gmail.com

Submitted 11 Agustus 2022 *Revised* 26 Februari 2023 *Accepted* 30 Maret 2023

Abstract. A potential alternative fuel option is biodiesel, which is produced mostly from natural resources due to the limited availability of petroleum supplies and environmental issues. Waste cooking oil (WCO) containing a high concentration of free fatty acid (FFA) can be transformed into biodiesel, which substantially benefits the environment and for reducing the fuel . The use of smectite clay as a catalyst in the esterification reaction of WCO with methanol was studied. Smectite was chemically activated by sulfuric acid (H_2SO_4) to obtain the acid-modified smectite. The utilization of an acid-catalyzed esterification procedure as a pre-treatment for WCO for biodiesel synthesis has been studied in some detail. However, there aren't many effective ways to optimize this operation. The process variables used in this study's esterification of FFAs in WCO were optimized using a Box-Behnken design (BBD). At atmospheric pressure, the catalyst amount of 5.03 wt%, the methanol to WCO molar ratio of 22.38, and the reaction time of 3.01 h are the optimal running parameters for accomplishing 97.96% FFA conversion. The catalyst was employed five times in a row without noticeably lowering its catalytic effectiveness. The results showed that smectite clay is an essential, low-cost, and recyclable catalyst for the esterification of FFA in WCO.

Keywords: Biodiesel, Smectite, Heterogeneous Catalyst, Box-Behnken Design, Esterification

INTRODUCTION

New sustainable energy solutions have evolved to replace society's massive reliance on limited fossil resources. Biodiesel is a type of biofuel that may be utilized in diesel engines without requiring significant modifications. Some advantages of biodiesel over fossil fuel include greater combustion efficiency, reduced carbon monoxide (CO) and hydrocarbon (HC) emissions, and increased lubricating capacity and oxygen content (Gonzaga et al. 2021). Biodiesel is composed of fatty acid alkyl esters (FAAEs) and is prepared by either transesterifying of triglycerides (TGs) or esterifying of free fatty acids (FFAs) with methanol in the addition of a catalyst to generate fatty acid methyl esters

DOI: 10.22146/ajche.77009

(FAMEs) and glycerol (Jeenpadiphat and Tungasmita 2014). Although vegetable oils are the most common source for biodiesel synthesis, additional fatty acid sources have been investigated, including waste cooking oils (WCOs), animal fats, and sewage sludge. Some feedstocks contain high quantities of FFA, up to 15 wt%. Because of this property, they are unsuitable for the typical direct base catalyzed process pathway to biodiesel owing to soap formation (Rezende and Pinto 2016). The extra step is required as a pre-treatment stage in order to lower the FFA concentration in WCO to less than 1 wt% within the allowed threshold before applying base-catalyzed transesterification. The esterification reaction of the FFA with alcohol is often performed sulfuric acid (H_2SO_4) as a homogeneous acid catalyst (Thoai et al. 2019).

Smectite clay minerals have a wide range of industrial applications, such as absorbents, catalysts, and nanocomposites, but they also pose significant scientific challenges. Treatments that include homoionic exchange, potentially heating or modification with acid, alkaline, or organic solutions, are required to tailor the smectite for specific applications. Because of octahedral and tetrahedral sheet substitutions, they exhibit a high degree of variability in the chemical structure and charge density of layer (Steudel et al. 2020). Figure 1 illustrates the crystal structure of smectite clays. Mineral acids may be used to increase smectite's surface activity (in terms of acidity) via activation. In this technique, metal ions are removed from the clay matrix and exchangeable positive ions (cationic species) are replaced with hydrogen ions (H^+) or protons (Altalhi et al. 2021, Negm et al. 2017). A novel heterogeneous acid-modified smectite catalyst was produced by chemically modifying smectite clay. The synthesized catalyst was utilized to catalyze WCO and methanol reactions. Optimizing the esterification conditions utilizing the developed catalyst.

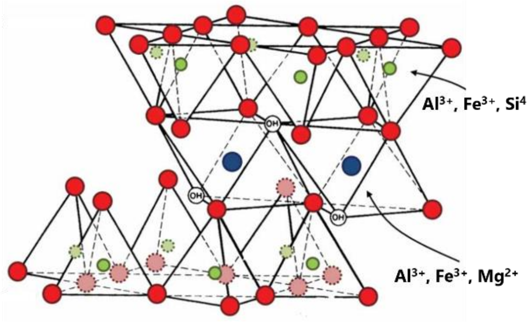

Fig. 1: Crystal Structure of Smectite Clays (Paineau et al. 2013, Bailey et al. 2020)

The response surface method (RSM), a statistical technique, is used to improve the operational parameters. It is used to evaluate many components and their interactions and to cut down on the number of necessary experimental trials to expedite and accurately conduct the experimental procedure. The Box-Behnken design (BBD) is one of the numerous accessible designs at RSM that have been used extensively to enhance biodiesel production. This is due to the fact that BBD can forecast, is more efficient at parameter tuning, and needs less trials than other designs (Ansori and Mahfud 2022).

The primary goal of this study is to apply the BBD approach to optimize the conditions for producing biodiesel from FFA in WCO via esterification using acid-modified smectite clay as a catalyst. The impacts of catalyst amount, methanol to WCO molar ratio, and reaction time are carefully considered. The research concluded with measurements of the fuel qualities of biodiesel synthesized under optimal conditions using American Society for Testing and Materials (ASTM) and European Standard (EN) standards.

MATERIALS AND METHODS

Materials

The smectite natural clay was obtained from Thai Green Agro, Bangkok, Thailand. WCO samples were taken at the campus cafeterias without being processed further. To obtain waste oil, the various fractions were blended. The non-oil materials of the WCO were separated using filter paper. Potassium hydroxide (KOH), H_2SO_4, methanol, ethanol and diethyl ether were analytical grade chemicals (Merck Ltd., Thailand, greater than 99% purity) that were used exactly as they were received.

Catalyst Preparation

The smectite clay was crushed and passed through sieve openings ranging from 150-250 μm. It was acidified in a round-bottom flask linked to a reflux condenser. Clay suspension containing 10% by weight in 4 mol/L H_2SO_4 was stirred for 2 h at 90 °C (Rezende and Pinto 2016). The sample was cleaned with distilled water and filtered under reduced pressure until the washing water's pH matched that of the original sample (6.8). The acid-modified smectite was dried in a 100 °C oven for 1 day before being ground untill it could pass through a 150-250 μm sieve opening. A desiccator was used to store the catalyst.

Catalyst Characterization

Powder X-ray diffraction (XRD) patterns of smectite clay were obtained using a LabX XRD-6100 (SHIMADZU, Japan) with Cu K_α radiation operating at 30 KV and 20 mA with a scanning rate of 4° in 2θ/min across a scan range of 2θ = 4-40°. Fourier transform infrared spectroscopy (FT-IR) was attained using a VERTEX 70v spectrometer (BRUKER, Germany) with a 4 cm^{-1} resolution between 400-4000 cm^{-1}. The sample morphology and elemental chemistry analyses at room temperature were also characterized using a Hitachi TM3030 (USA) scanning electron microscopy (SEM) equipment outfitted with an energy dispersive spectroscopy (EDS) detector. To prevent electric current induction. The material was coated with gold (Au) using a sputter coater to prevent electric current induction. The working distance was 14-15 mm, and the accelerating voltage was 15 kV.

Esterification (Pre-treatment) Process

The appropriate amounts of WCO, methanol, and modified smectite clay catalyst were added to a 250 mL round-bottom flask, directly attached to a reflux condenser and placed in a constant-temperature heating bath (60 °C). At atmospheric pressure, the suspension was continuously stirred by a 200 rpm magnet. After the reaction, the mixture was cooled and then centrifuged to separate the used catalyst from the liquid phase. Titration was used to figure out how much FFA in WCO was turned into biodiesel (Diaz-Felix et al. 2009, Photaworn et al. 2017). The percentage of conversion was calculated using Eq. (1).

$$\%Conversion = \frac{FFA_i - FFA_t}{FFA_i}\mathrm{x}100 \qquad (1)$$

Upon completion of the esterification process, the smectite clay was recovered. It was removed from the reaction mixture by filtering and washing three times with n-hexane (Wang et al. 2022). The previously used catalyst was employed in the following run under similar reaction conditions.

Box-Behnken Design for Optimization

Statistical approaches, namely the RSM,

were applied to track and demonstrate the best settings for the esterification (pre-treatment) process in order to optimize FFA conversion in WCO. This RSM uses quantitative data from operations to create linear regression models and optimize responses that are impacted by a number of variables (Marwaha et al. 2020, Ansori and Mahfud 2022). The three parameters carefully chosen for statistical analysis were the catalyst amount (A), the methanol to WCO molar ratio (B), and the reaction time (C). A three-level, three-factor of BBD was used in this study to create a total of 15 experimental runs. The Design-Expert® Software version 13 (Stat-Ease, Inc., Minneapolis, MN, USA) developed a quadratic polynomial equation. The analysis of variance (ANOVA) test was performed to evaluate the mathematical equation model's fit.

Biodiesel Characterization

Kinematic viscosity, density, flash point, cloud point, pour point, acid value, and moisture content were determined and quantified for biodiesel using ASTM and EN standards. All values were compared to those specified in the United States biodiesel standard (ASTM D-6751) and the European biodiesel standard (EN 14214).

RESULTS AND DISCUSSION

The mineral composition of smectite natural clay (SME_{nat}) may be determined by XRD using the Inorganic Crystal Structure Database (ICSD) standard and the location of 2-theta (Syukri et al. 2020). Figure 2 shows it to make it clear that the materials are crystalline and in the crystal phase. The XRD pattern revealed that the samples contained montmorillonite, quartz, and feldspar.

Because of the smectite's surface acidity, H_2SO_4 probably actually reacted with the montmorillonite and feldspar phases, destroying crystallinity (Wang et al. 2022). This is indicated by the fact that the intensity of these peaks significantly decreased when compared to natural clay diffraction peaks, especially at 2θ = 5.7° and 27.7°.

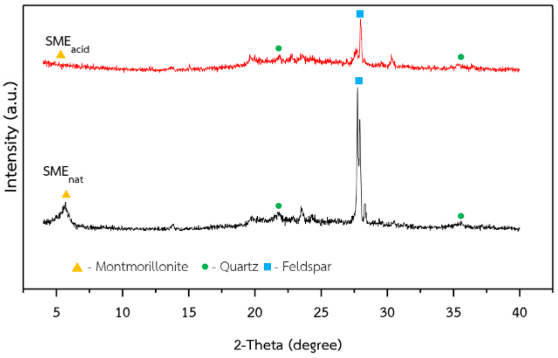

Fig. 2: XRD Patterns of Natural Clay (SME_{nat}) and Acid-modified Clay (SME_{acid})

The FTIR spectrum of the smectite natural clay (Figure 3) shows the appearance of functional groups including Al–O–H and Mg–O–H stretching (3622 cm^{-1}), H–O–H stretching (3400 cm^{-1}), H–O–H bending (1670 cm^{-1}), Si–O–Si stretching (1037 cm^{-1}), O–H bending bounded Al^{3+} and Fe^{3+} (932 cm^{-1}), and Si–O stretching (790 cm^{-1}). Addition of H_2SO_4 modified the crystallinity phase of the smectite structure, according to FTIR analysis. With acid loading, the intensity of the Al–O–H and Mg–O–H stretching group reduced. Furthermore, a shift in this group's absorption band from 3614 cm^{-1} to lower wavenumbers suggested the existence of the newly discovered functional Al–O–K group in the clay catalysts under investigation (Soetaredjo et al. 2011).

SEM was used to identify the morphology of natural and acid-modified smectite surfaces, as shown in Figure 4. It has been found that natural clay has been observed to be foliated and flaky in form.

After H_2SO_4 modification, it becomes fluffier and slightly larger porous aggregates, indicating cation exchange between the clay and the relevant metal. This reduces the amount of amorphous phase and may provide effective bonding sites, allowing for agglomeration. Moreover, the XRD pattern shows a somewhat lower peak intensity than untreated clay (Munir et al. 2022).

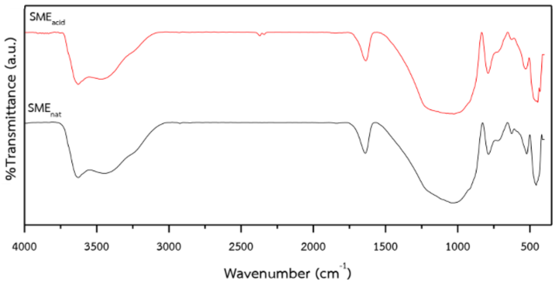

Fig. 3: FTIR Spectra of Natural Clay (SME_{nat}) and Acid-modified Clay (SME_{acid})

The elemental characterization of the clay was identified using EDS, a well-known analytical technique for determining the elemental composition of a material (Figure 5). A specific color can identify an X-ray within an inspection field. The weight percent (norm. wt.%) of aluminum (Al), magnesium (Mg), silicon (Si), calcium (Ca), sodium (Na), potassium (K), carbon (C), and oxygen (O) on a specific area of the catalyst's surface was found to be 6.59, 1.11, 24.47, 0.12, 1.20, 1.48, 11.60, and 53.42 %, respectively. The presence of metal oxide in clay improves its catalytic activity and serves as a transformer during the esterification reaction (Buasri and Loryuenyong 2018, Munir et al. 2022).

The experiments were carried out to analyze the data with an ANOVA using an RSM based on BBD that takes three input variables to generate a quadratic equation model. The best results were achieved with a risk level of 0.1 and a confidence level of

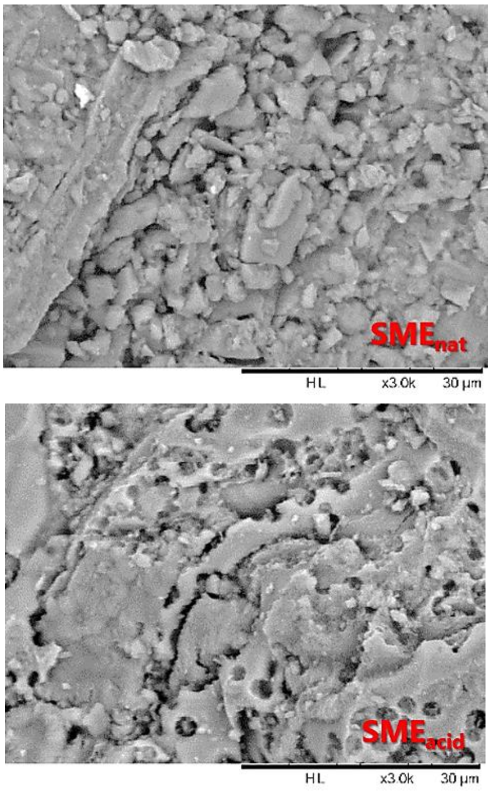

Fig. 4: SEM Images of Natural Clay (SME_{nat}) and Acid-modified Clay (SME_{acid})

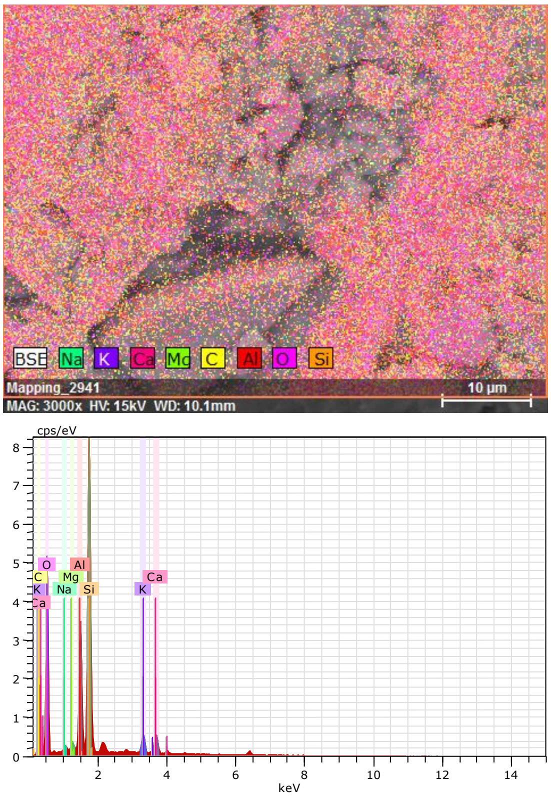

Fig. 5: EDS Analysis of Acid-modified Clay

95% for highly significant models (Marwaha et al. 2020). Table 1 displays the characteristics of the selected factors: catalyst amount (A), methanol to WCO molar ratio (B), and reaction time (C), as defined for the RSM analysis. Table 2 summarizes 15 different experimental runs that were accomplished by changing the reaction conditions. It shows the response %conversion values that were collected from several experiments conducted, both experimental and forecasted.

The coefficients and statistical significance of the whole regression model equation were calculated and analyzed using Design-Expert® Software version 13. Eq. (2) represents the quadratic regression model used to predict the percentage of FFA conversion in WCO.

$$Y = 88.60 + 0.9775A + 23.84B + 4.90C - 5.59A^2 - 13.94B^2 - 3.71C^2 + 4.00AB - 0.863AC - 3.06BC \quad (2)$$

Table 1. Description of Independent Input Parameters

Abbreviation	Factor	Units	Low level (-1)	Middle level (0)	High level (+1)
A	Catalyst amount	wt%	4	5	6
B	Methanol to WCO molar ratio	mol:mol	16	20	24
C	Reaction time	h	2	3	4

Table 2. Experimental Conversion of 15 Runs Using BBD

Run	Catalyst amount (wt%)	Methanol to WCO molar ratio (mol:mol)	Reaction time (h)	Experimental conversion (%)	Predicted conversion (%)
1	4	16	3	47.51	48.24
2	6	20	2	76.33	76.23
3	4	24	3	89.10	87.93
4	5	20	3	88.82	88.60
5	5	20	3	88.13	88.60
6	5	20	3	88.84	88.60
7	6	16	3	41.02	42.19
8	5	24	4	95.55	96.63
9	4	20	4	83.98	84.08
10	5	24	2	92.11	92.94
11	4	20	2	72.21	72.55
12	5	16	4	55.89	55.06
13	6	20	4	84.65	84.31
14	6	24	3	98.62	97.89
15	5	16	2	40.21	39.14

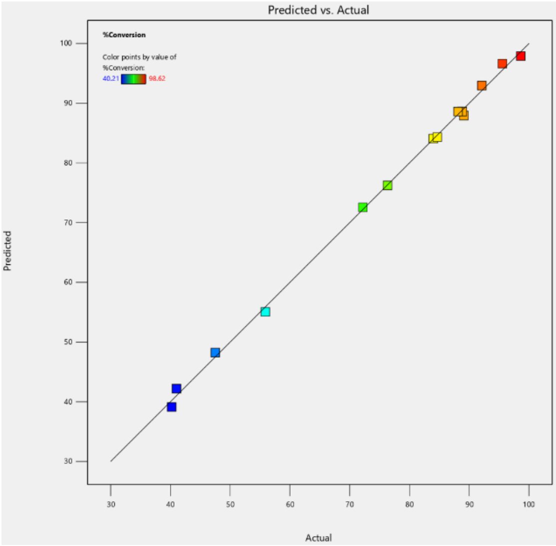

Fig. 6: Plot of Experimental and Predicted %Conversion

The experimental findings are shown in comparison to the data that the empirical model predicted in Figure 6. The determination coefficient (R^2) and the adjusted determination coefficient (R^2_{adj}) were 0.9986 and 0.9960, respectively. The high values of both coefficients confirm the model's high significance and justify an excellent correlation between the independent variables. The coefficient of variation was 1.67% in the meanwhile. The comparatively low value of the coefficient of variation indicates that this fitted model is more reliable (Chumuang et al. 2017, Danane et al. 2022).

3D surface plots are used to show how reaction parameter effects affect the %FFA conversion in WCO. Figure 7 depicts the interactions between the amount of catalyst and the methanol to WCO molar ratio on the %FFA conversion at a constant reaction time. The slope of the surface determines the degree to which these factors influence %conversion of FFA in WCO. At the beginning stage, the higher the slope of the surface of the catalyst amount, the greater the influence of this variable over the methanol to WCO molar ratio. This finding demonstrated the significance of the acid-modified smectite catalyst in the esterification reaction. But increasing the amount of catalyst to 6 wt% seems to slow

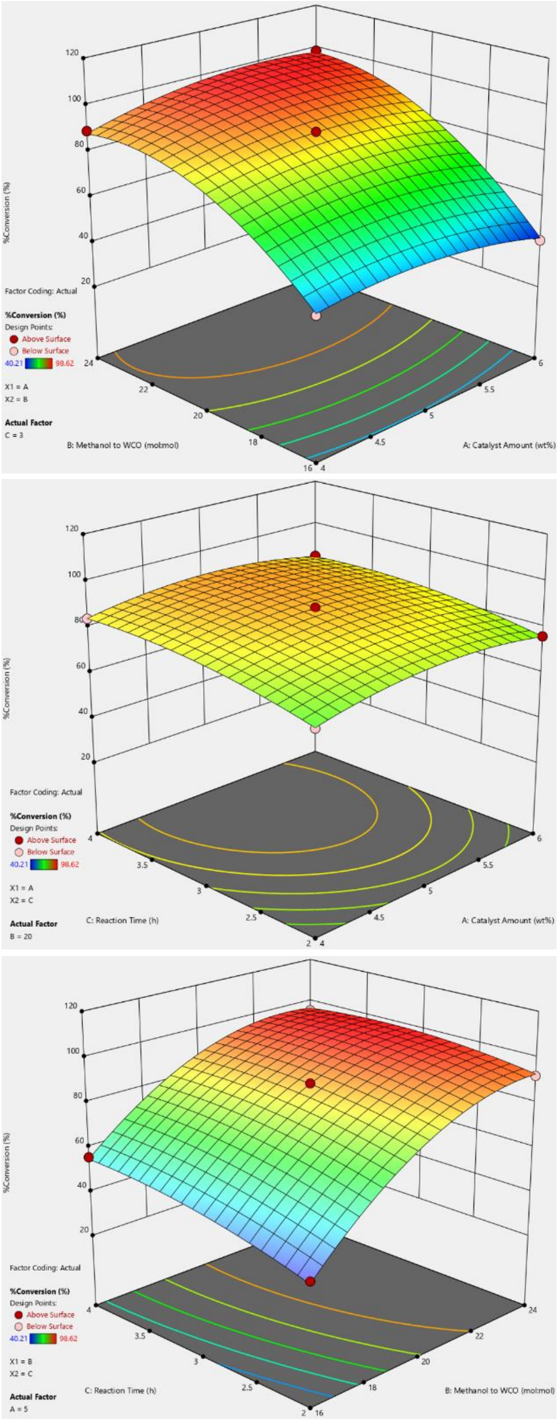

Fig. 7: RSM Plots of the Catalyst Amount, Methanol to WCO Molar Ratio, and Reaction Time Effects on Conversion

down the reaction rate because of the hydrolysis reaction that happens when water is present (Thoai et al. 2019). Furthermore, biodiesel that is too viscous to be used as an engine fuel can be produced by adding too much catalyst content (Razzaq et al. 2022).

The esterification reaction had a stoichiometric molar ratio of 1:1 (alcohol: FFA), but in actuality, an excess of methanol was required to shift the reaction equilibrium to the synthesis of biodiesel products. The molar ratio was raised, which enhanced the %conversion of FFA. Increases in the molar ratio of methanol to WCO above 24 marginally reduced the consequent% FFA conversion, possibly because the excess methanol reduced the sulfonic group's catalytic effectiveness (Jeenpadiphat and Tungasmita 2014).

This chart illustrates the %conversion from WCO through esterification reaction at various reaction times, ranging from 2 to 4 h. Before reaching equilibrium, the forward reaction, or biodiesel production, was swift in the early steps of the esterification reaction. However, the backward reaction began after others continued past the ideal reaction time. As a result, a prolonged reaction time decreases the FFA conversion rate (Degfe et al. 2019).

On the basis of the limit criteria of reaction conversion maximization, the optimum reaction conditions were determined using a regression model (Eq. (2)), the amount of catalyst consumed, the molar ratio of methanol to WCO, and reaction time minimization, as shown in Figure 8. A catalyst amount of 5.02734 wt%, a methanol to WCO molar ratio of 22.3803, and a reaction time of 3.00898 h are optimal for achieving 97.9628% FFA conversion. Hence, the RSM model was deemed accurate and trustworthy for forecasting the conversion of reactive FFA. These findings are equivalent to those attained by Mostafaei et al. (2015) and Moyo et al. (2021).

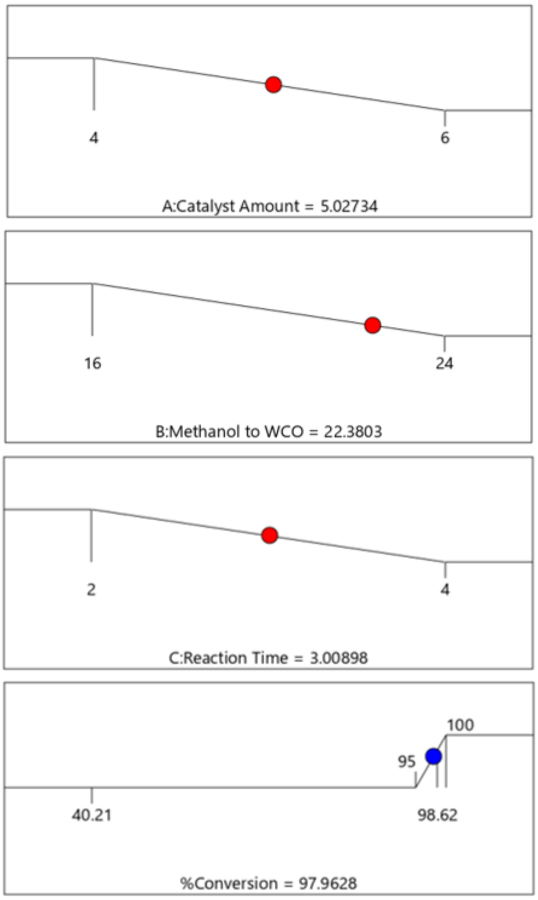

Fig. 8: Optimal Reaction Conditions

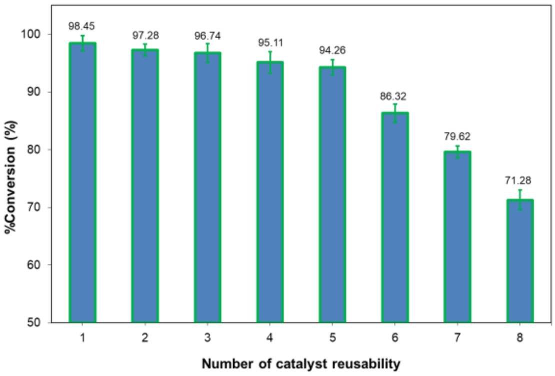

Fig. 9: Effect of Reusability of Acid-modified Smectite Clay Catalyst on the %Conversion (Catalyst Amount 5.03 wt%, Methanol to WCO Molar Ratio 22.38, and Reaction Time 3.01 h)

Catalyst recycling is a key step since it reduces the total cost of the biodiesel production process. Previous research has shown that heterogeneous catalysts can be recycled and have good recyclability (Buasri et al. 2016). The utilized catalyst was retested for 3.01 h and 5.03 wt% catalyst amount at 22.38 methanol to WCO molar ratio. Figure 9 summarizes the findings of acid-modified smectite catalyst's recycling investigations. It was discovered that the clay catalyst could be recycled for up to five subsequent reactions, and the %FFA conversion was around 98.45-94.26%. As a consequence of the inactivation of catalyst active sites, the %conversion decreased with each successive cycle, falling to 79.62% and 71.2%, respectively, in the sixth and seventh reactions. During the esterification process, several of the potential acid sites were poisoned. Table 3 demonstrates that the new catalyst's reusability and catalytic activity were within the range reported by previous studies.

Biodiesel must agree to a number of requirements outlined in biodiesel standards, particularly the American biodiesel standard (ASTM D-6751) and the European biodiesel standard (EN14214), in order to be utilized in diesel engines. Table 4 summarizes the physical, chemical and fuel properties of biodiesel obtained in this study and compares them to the approved biodiesel international standards ASTM D-6751 and EN14214. It is obvious that a large number of its features fall within the range of fuel properties that are outlined in the most recent biodiesel standards (Buasri and Loryuenyong 2015).

Table 3. Reusability and Catalytic Activity Comparison Between Material-derived Catalysts

Catalyst	Repeat run number	Remained catalytic activity (%)	References
Smectite	5	94	This work
Smectite	3	97	Alves et al. (2014)
Bentonite	3	85	Soetaredjo et al. (2011)
Bentonite	5	80	Wang et al. (2022)
Montmorillonite	5	77	Munir et al. (2021)
Metakaolinite	8	84	Ramirez-Ortiz et al. (2012)
Dolomite	5	94	Buasri et al. (2016)

Table 4. Fuel Properties of Biodiesel

Fuel property	Value	ASTM D-6751	EN14214
Kinematic viscosity (mm^2/s)	4.28	1.0-6.0	3.5-5.0
Density (g/cm^3)	0.889	Not specified	0.860-0.900
Flash point (°C)	165	130 Minimum	120 Minimum
Cloud point (°C)	15	Not specified	Not specified
Pour point (°C)	9	Not specified	Not specified
Acid value (mg KOH/g oil)	0.40	0.8 Maximum	0.5 Maximum
Moisture content (%)	0.022	0.050 Maximum	0.050 Maximum

CONCLUSIONS

The treatment of smectite clay with H_2SO_4 was effective and produced novel catalysts with high catalytic activity for the esterification of FFA in WCO with methanol during biodiesel synthesis. A three-factor, three-level BBD was used to maximize maximize the conversion of FFA succesfully. Using the second order polynomial equation, the most significant effects of these components at different levels on the response (%conversion) may be estimated. The quadratic RSM investigated aided in determining the interaction impacts of these three components. The validation of the optimization technique confirmed the model's applicability and adjustability. Following the optimal conditions of 5.03 wt% catalyst amount, 22.38 methanol to WCO molar ratio, and 3.01 h reaction time, a maximum of 97.96% FFA conversion was achieved. The optimization study was determined to be beneficial in terms of making the biodiesel manufacturing process more cost-effective. Additionally, using the modified smectite clay catalyst provides significant environmental advantages since it is naturally occurring, affordable, and widely accessible.

ACKNOWLEDGEMENT

The authors would also like to acknowledge the Department of Materials Science and Engineering (MATSE), Faculty of Engineering and Industrial Technology (EnTech) at Silpakorn University (SU) for their assistance and encouragement with this project.

AUTHOR CONTRIBUTIONS

All of the authors collaboratively created this work. Achanai Buasri conceptualized the experiments, data analysis, and wrote the first draft and thoroughly revised the manuscript. Suthita Lertnimit, Arnon Nisapruksachart and Issara Khunkha performed the experiments in the laboratory. Vorrada Loryuenyong contributed to the conceptual approach and results discussion, and approved the final version of the revised manuscript.

NOMENCLATURE

FFA_i : initial FFA content [wt%]
FFA_t : FFA content at any time [wt%]
$R^2{}_{adj}$: adjusted determination coefficient
R^2 : determination coefficient
Y : response variable of %conversion [%]
A : actual values of the predicted catalyst amount
B : actual values of the predicted methanol to WCO molar ratio
C : actual values of the predicted reaction time

REFERENCES

Altalhi, A. A., Mohamed, E. A., Morsy, S. M., Kana, M. T. H. A., and Negm, N. A., 2021. "Catalytic manufacture and characteristic valuation of biodiesel-biojet achieved from Jatropha curcas and waste cooking oils over chemically modified montmorillonite clay," *J. Mol. Liq., 340,* 117175.

Alves, H. J., Rocha, A. M., Monteiro, M. R., Moretti, C., Cabrelon, M. D., Schwengber, C. A., and Milinsk, M. C., 2014. "Treatment of clay with KF: New solid catalyst for biodiesel production," *Appl. Clay Sci., 91-92,* 98-104.

Ansori, A., and Mahfud, M., 2022. "Box-Behnken design for optimization on biodiesel production from palm oil and methyl acetate using ultrasound assisted interesterifcation method," *Period. Polytech. Chem. Eng., 66,* 30-42.

Bailey, L., Lekkerkerker, H. N. W., and Maitland, G. C., 2015. "Smectite clay - inorganic nanoparticle mixed suspensions: Phase behaviour and rheology," *Soft Matter, 11,* 222-236.

Buasri, A., and Loryuenyong, V., 2015. "The new green catalysts derived from waste razor and surf clam shells for biodiesel production in a continuous reactor," *Green Process. Synth., 4,* 389-397.

Buasri, A., and Loryuenyong, V., 2018. "Continuous production of biodiesel from rubber seed oil using a packed bed reactor with $BaCl_2$ impregnated CaO as Catalyst," *Bull. Chem. React. Eng. Catal., 13,* 320-330.

Buasri, A., Lukkanasiri, M., Nernrimnong, R., Tonseeya, S., Rochanakit, K., Wongvitvichot, W., Masa-ard, U., and Loryuenyong, V., 2016. "Rapid transesterification of *Jatropha curcas* oil to biodiesel using novel catalyst with a microwave heating system," *Korean J. Chem. Eng., 33,* 3388-3400.

Chumuang, N., and Punsuvon, V., 2017. "Response surface methodology for biodiesel production using calcium methoxide catalyst assisted with tetrahydrofuran as cosolvent," *J. Chem., 2017,* Article ID 4190818.

Danane, F., Bessah, R., Alloune, R., Tebouche, L., Madjene, F., Kheirani, A. Y., and Bouabibsa, R., 2022. "Experimental optimization of waste cooking oil ethanolysis for biodiesel production using response surface methodology (RSM)," *Sci. Tech. Energ. Transition, 77,* 14.

Degfie, T. A., Mamo, T. T., and Mekonnen, Y. S., 2019. "Optimized biodiesel production from waste cooking oil (WCO) using calcium oxide (CaO) nanocatalyst," *Sci. Rep., 9,* 18982.

Diaz-Felix, W., Riley, M. R., Zimmt, W., and Kazz, M., 2009. "Pretreatment of yellow grease for efficient production of fatty acid methyl esters," *Biomass Bioenerg., 33,* 558-563.

Gonzaga, V. E., Romero, R., Gómez-Espinosa, R. M., Romero, A., Martínez, S. L., and Natividad, R., 2021. "Biodiesel production from waste cooking oil catalyzed by a bifunctional catalyst," *ACS Omega, 6,* 24092-24105.

Jeenpadiphat, S., and Tungasmita, D. N., 2014. "Esterification of oleic acid and high acid content palm oil over an acid-activated bentonite catalyst," *Appl. Clay Sci., 87,* 272-277.

Marwaha, A., Rosha, P., Mohapatra, S. K., Sunil Kumar Mahla, S. K., and Dhir, A., 2019. "Biodiesel production from *Terminalia bellerica* using eggshell-based green catalyst: An optimization study with response surface methodology," *Energy Rep., 5,* 1580-1588.

Mostafaei, M., Ghobadian, B., Barzegar, M., and Banakar, A., 2015. "Optimization of ultrasonic assisted continuous production of biodiesel using response surface methodology," *Ultrason. Sonochem., 27,* 54-61.

Moyo, L. B., Iyuke, S. E., Muvhiiwa, R. F., Simate, G. S., and Hlabangana, N., 2021. "Application of response surface methodology for optimization of biodiesel production parameters from waste cooking oil using a membrane reactor," *S. Afr. J. Chem. Eng., 35,* 1-7.

Munir, M., Ahmad, M., Rehan, M., Saeed, M., Lam, S. S., Nizami, A. S., Waseem, A., Sultana, S., and Zafar, M., 2021. "Production of high quality biodiesel from novel non-edible *Raphnus raphanistrum* L. seed oil using copper modified montmorillonite clay catalyst," *Environ. Res., 193,* 110398.

Munir, M., Saeed, M., Ahmad, M., Waseem, A., Sultana, S., Zafar, M., and Srinivasan, G. R., 2022. "Optimization of novel *Lepidium perfoliatum* Linn. biodiesel using zirconium-modified montmorillonite clay catalyst," *Energ. Source Part A, 44,* 6632-6647.

Negm, N. A., Sayed, G. H., Yehia, F. Z., Habib, O. I., and Mohamed, E. A., 2017. "Biodiesel production from one-step heterogeneous catalyzed process of *Castor* oil and *Jatropha* oil using novel sulphonated phenyl silane montmorillonite catalyst," *J. Mol. Liq., 234,* 157-163.

Paineau, E., Philippe, A. M., Antonova, K., Bihannic, I., Davidson, P., Dozov, I., Gabriel, J. C. P., Impéror-Clerc, M., Levitz, P., Meneau, F., and Michot, L. J., 2013. "Liquid–crystalline properties of aqueous suspensions of natural clay nanosheets," *Liq. Cryst. Rev., 1,* 110-126.

Photaworn, S., Tongurai, C., and Kungsanunt, S., 2017. "Process development of two-step esterification plus catalyst solution recycling on waste vegetable oil possessing high free fatty acid," *Chem. Eng. Process: Process Intensif., 118,* 1-8.

Ramirez-Ortiz, J., Martinez, M., and Flores, H., 2012. "Metakaolinite as a catalyst for biodiesel production from waste cooking oil," *Front. Chem. Sci. Eng., 6,* 403-409.

Razzaq, L., Abbas, M. M., Miran, S., Asghar, S., Nawaz, S., Soudagar, M. E. E., Shaukat, N., Veza, I., Khalil, S., Abdelrahman, A., and Kalam, M. A., 2022. "Response surface methodology and artificial neural networks-based yield optimization of biodiesel sourced from mixture of palm and cotton seed oil," *Sustainability, 14,* 6130.

Rezende, M. J. C., and Pinto, A. C., 2016. "Esterification of fatty acids using acid-activated Brazilian smectite natural clay as a catalyst," *Renew. Energy, 92,* 171-177.

Soetaredjo, F. E., Ayucitra, A., Ismadji, S., and Maukar, A. L., 2011. "KOH/bentonite catalysts for transesterification of palm oil to biodiesel," *Appl. Clay Sci., 53,* 341-346.

Steudel, A., Friedrich, F., Boháč, P., Lieske, W., Baille, W., König, D., Schuhmann, R., and Emmerich, K., 2020. "Equimolar cation exchange of polyacrylamide in smectite," *Appl. Clay Sci., 188,* 105501.

Syukri, S., Septioga, K., Arief, S., Putri, Y. E., Efdi, M., and Septiani, U., 2020. "Natural clay of Pasaman Barat enriched by CaO of chicken eggshells as catalyst for biodiesel production," *Bull. Chem. React., 15,* 662-673.

Thoai, D. N., Hang, P. T. L., and Lan, D. T., 2019. "Pre-treatment of waste cooking oil with high free fatty acids content for biodiesel production: An optimization study via response surface methodology," *Vietnam J. Chem., 57,* 568-573.

Wang, Y., Muhammad, Y., Yu, S., Fu, T., Liu, K., Tong, Z., Hu, X., and Zhang, H., 2022. "Preparation of Ca- and Na-modified activated clay as a promising heterogeneous catalyst for biodiesel production via transesterification," *Appl. Sci., 12,* 4667.