

Transforming Low-cost Mineral Clay to Proper Catalyst for Biodiesel Production from Transesterification of Triglycerides in Methanol

Dang Tan Hiep, Bing-Hung Chen*

Department of Chemical Engineering, National Cheng Kung University, Tainan 70101 Taiwan

*Corresponding Author's E-mail: bkchen@mail.ncku.edu.tw

Abstract

In this study, a clay catalyst prepared from hydrothermal activation of kaolin clay was employed to catalyze transesterification of triglycerides in excess methanol for biodiesel production. The optimal condition for transformation of kaolin to catalyst is found at an aging time of 24 h and a mass ratio of calcined kaolin and sodium hydroxide at 1:2. Various instruments such as XRD, FT-IR, SEM, EDS, and TGA were applied to characterize the as-prepared catalyst. The obtained catalytic material was advantageous not only in easy preparation, but also as a low-cost solid catalyst that can effectively catalyze transesterification of triolein in excess methanol for production of methyl oleate as biodiesel. High conversion efficiency, $(93.9 \pm 6.0) \%$, of triolein to methyl oleate was attained under optimal conditions of transesterification process.

Keywords: Biodiesel, clay catalyst, kaolin, transesterification, triolein, methyl oleate.

NSC Project no.: NSC 100-3113-E-006-016

1 Introduction

Recently, biodiesel has been alternatively using to prevent problems of human and environment from consummation of non-renewable energy sources as fossil fuels [1, 2].

Catalysts are usually used to achieve high conversion and reduce reaction time of transesterification process [3] of animal fats [4], vegetable [5]/waste frying oils [6]. However, most of them have some disadvantages such as difficulty in separation main from by-products as using homogeneous catalyst [1] and charging high cost of resins

[7] or enzymes [8]. Therefore, new catalysts are introduced to overcome these obstacles.

In our point of view, natural and modified clay minerals have been promising to satisfy the needs of us. Recently, several researchers have been working on investigation catalytic activity of clay minerals particularly zeolites and kaolin in synthetic organic field [9-12] and application kaolin as a precursor for ceramic production [13]. Nevertheless, there are still few articles relate to application of kaolin as solid catalyst for catalyzing biodiesel production via transesterification reaction. In this case, a solid, low-cost as-synthesized catalyst prepared in a simple method from kaolin was employed to let the transesterification of triolein and methanol go to side of products. Additionally, methanol was used as reactants to reduce product's price.

Design of experiments (DOE) is usually applied to experimental science and engineering fields because of its advantages as reducing costs and time for experiments [14]. It begins with defining of a problem, choosing appropriate variables, gathering and interpreting of experimental results, fitting and optimizing the model [15]. In this lab-scale work, a response surface methodology namely Box-Behnken design [16] was employed to find out the optimal conditions of independent variables of the transesterification reaction of triolein and methanol because of in requiring a few number of experiments compared to factorial or central composite design [16].

2 Experimental section

2.1 Chemicals and Catalyst preparation

Triolein (~65%) was supplied by Sigma-Aldrich®. CH₃OH

and NaOH (pellet form) were of analytical standard reagents. Parent kaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) is one of products of J. T. Baker Company. The raw powder kaolin was calcined at 800 °C during 10 h to attain calcined kaolin (CK) using a programmable furnace with ramping rate of temperature to be of 5 °C/min. Then, it was treated with NaOH in a mass ratio of CK:NaOH at 1:2 to obtain transformation kaolin (TK) via hydrothermal method. This preparation was performed in a three-neck-flask reactor put in a temperature controlled jacket, and placed on a magnetic controlled machine. The reaction mixture was heated at reflux at 90 °C, and 600 rpm of rotating speed during 24 h subsequently quenched by cool water for stopping reaction. After settling, the slurry was carefully decanted. Additionally, the obtained solid was dried in an air oven at 110 °C for 24 h before calcination at 400 °C for 6 hours.

2.2 Instruments

Crystallinity, functional groups and morphology of as-prepared catalyst were characterized by using XRD, FT-IR and SEM. XRD analyses were done on Rigaku Ultima diffractometer with Cu K α radiation at 40 kV and 20 mA and followed settings of step interval at 0.01°, 2 θ =5°-70° and 4 °/min of speed rate of scanning. Moreover, a Varian 2000 FT-IR using the KBr pellet technique was also conducted to record functional groups of materials in a wavenumber range of 4000-400 cm⁻¹ via a Varian 2000 FT-IR (Scimitar Series). Furthermore, the internal structure of these materials was recorded by using a scanning electron microscopy (SEM, Jeol JSM-6700F).

2.3 Transesterification of triglycerides and sample analyses

Conversion efficiency of triglycerides to fatty acid methyl esters (FAMES) as biodiesel was used to evaluate catalyst efficacy. Transesterification of triolein in excess CH_3OH catalyzed by NaOH-activation kaolin were carried out in a vial sealed by a Teflon cap. Then, the batch reactor was placed in a temperature controlled water bath over a magnetic controlled stirrer/hot plate. The mixture was continuously run to desired time, while reaction temperature and agitation speed were constantly kept at 63 °C and 600 rpm, respectively. Solid catalyst was easily separated from the mixture by centrifugation at 4000 rpm

during 20 minutes. After separating, the liquid phase was transfer to a rotary vacuum evaporator to separate by-products and main products.

Biodiesel mixture was analyzed via utilization of a GC-FID (Shimadzu GC-2014 with a DB-5 column as $12\text{ m} \times 0.32\text{ mm} \times 0.1\text{ }\mu\text{m}$). Finally, the conversion efficiency of reaction was calculated by using the equation in the published literature [17]. The GC-FID analysis in biodiesel conversion is regularly validated by $^1\text{H-NMR}$.

3 Results and discussions

3.1 Preparation and characterization of catalysts

XRD patterns. In *Figure 1a*, the characteristic signals of raw kaolin were completely disappeared at those thermal treatment conditions. It would be understood that there was a completely breakdown of crystalline structure of calcined kaolin in comparing with mother form. A new broad band in range of $20^{\circ} < 2\theta < 30^{\circ}$ which assigned to amorphous phase of SiO_2 [18] took place at those setting temperatures of calcination, *Figure 1a*. It was consistent with the results of *Lenarda, M., et al. (2007)* [18]. The remaining peaks could be mentioned as traces as mica, quartz [18].

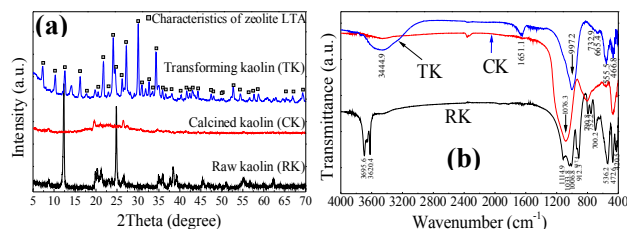


Figure 1: The XRD patterns (a) and FT-IR spectra (b) of raw, calcination and transformation kaolin.

Fourier transform infrared spectroscopy (FT-IR). The FT-IR characterization of parent, calcined and transformed kaolin which activated with sodium hydroxide are shown in *Figure 1b*. The CK and TK have a broad O-H stretching band and an adsorption band in range of 3700 to 3000 cm^{-1} and near 1650 cm^{-1} , respectively [19]. These peak bands mean these materials are a hydrate. The two adsorption bands at 1413 cm^{-1} and 1450.5 cm^{-1} belong to carbonate group. It is probably consequence of absorbing carbon dioxide in the air during preparation of sample [20]. Besides, it can be explained by a reaction of sodium oxide with carbon dioxide in ambient air. The most characteristic of kaolin (1114.9 cm^{-1}) was completely disappeared as doing calcination at 800 °C. This conclusion is also consistent of that of XRD. *Figure 1a*. Band at 1076.3 cm^{-1}

of CK shifted to 997.2 cm^{-1} assigned to asymmetric Al-O vibrations. Intensity of bands at 557.4 cm^{-1} increased and shifted to 555.5 cm^{-1} , while that of band at 474.5 cm^{-1} decreased and shifted to lower wavenumber, 466.8 cm^{-1} . These phenomena could be explained by more substitution of Al in tetrahedral sites [21].

SEM analyses. Figure 2 illustrated morphology of RK, CK and TK forms. The parent kaolin was formation of stacking of flaky particles with rough surface, Figure 2a. After calcination at $800\text{ }^{\circ}\text{C}$, the obtained kaolin was amorphous form, Figure 2b. In SEM micrographs of transformed kaolin, Figure 2c, shape of particles on the surface at magnifications of $10000\times$ looks like cubic. Those particles were arranged by agglomerating layer by layer.

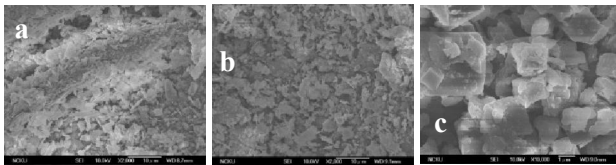


Figure 2: SEM micrographs of raw (a), calcined at $800\text{ }^{\circ}\text{C}$ (b) and transformed kaolin (c).

In conclusion, the obtained material is similar to zeolite LTA (hydrated form) [21, 22].

3.2. Optimization of biodiesel production process

A Box-Behnken design was applied to optimize conditions of biodiesel production via transesterification of triolein in excess methanol catalyzed by as-prepared catalyst. The levels and factors were listed in Table 1. Each coded factor has three levels (± 1 and 0). They stand for experimental conditions at axes and central point.

Table 1: Levels of chosen independent variables of the Box-Behnken design

(Uncoded, Coded variable)	Name of factors	Levels		
		Low (-1)	Center (0)	High (+1)
(U_1, X_1)	Methanol to oil ratio, wt./wt.	20.0	35.0	50.0
(U_2, X_2)	Reaction temperature, $^{\circ}\text{C}$	50.0	63.0	76.0
(U_3, X_3)	Reaction time, min	40.0	110.0	180.0
(U_4, X_4)	Catalyst loadings, wt.% of oil	50.0	75.0	100.0

After doing interpretation on a total of 27 randomly runs, the most important effect is mass ratio of methanol to oil. Then, two-way interaction between mass ratio of methanol to oil and reaction time (X_1X_3) and quadratic interaction of reaction temperature (X_2^2) are also strong significant at

p -value of 0.05. Reaction time (U_3, X_3), catalyst loadings (U_4, X_4) and two square interactions (X_1^2, X_4^2) should be also significant.

Furthermore, an analysis of variance (ANOVA) was conducted and indicated that the full obtained model was significantly suitable for predicting experiment results, p -value of lack-of-fit equaled to 0.99%.

Optimization for biodiesel production variables. There is a unique optimum combination of factor values and that surface is shaped like a saddle point. Moreover, the stationary point of this design is located at coordinates of natural and coded variables ($36.55:1$, $63.0\text{ }^{\circ}\text{C}$, 146.0 min and $72.0\text{ wt.}\%$ of oil), and ($X_1 = 0.1034$, $X_2 = -0.0074$, $X_3 = 0.5137$ and $X_4 = -0.1178$), respectively. Under this condition, the conversion was maximal at $(93.9 \pm 6.0)\%$. Three confirmation experiments were conducted under the optimal condition to verify the quadratic response surface model could satisfactorily describe the yield or not. The average value was $(92.8 \pm 4.0)\%$. It revealed 1.15% difference between observed and calculated values. Therefore, this model could be well applied to predict results in this study.

4 Conclusions

A solid, low-cost as-synthesized catalyst was successfully applied for biodiesel production from triolein with methanol. The optimum conditions of preparation were of 1:2 in weight ratio between calcined kaolin and sodium hydroxide during 24 h of exposure. The transformed kaolin has characteristics of Linde type A (LTA, hydrate form).

The optimal condition to produce biodiesel, in this case, follows: $36.55:1$ in feed ratio of methanol/oil, 146 minutes and 72 wt.% based on oil of reaction time and catalyst loadings, respectively.

Under this condition, the high conversion efficiency, $(93.9 \pm 6.0)\%$, of biodiesel production from triolein and methanol could be attained.

Acknowledgments

This work was financially supported by the National Science Council of Taiwan (NSC 100-3113-E-006-016). Furthermore, authors would like to thank Ms. Jenny Wu of the NCKU Instrument Center for her assistance in NMR

operations.

References

- [1] Juan A. Melero, *et al.* "Heterogeneous acid catalysts for biodiesel production: current status and future challenges", *Green Chemistry*, **11**, pp. 1285-1308, 2009.
- [2] Jiri Jaromír Klemes, *et al.* "Minimising emissions and energy wastage by improved industrial processes and integration of renewable energy", *Journal of Cleaner Production*, **18**, pp. 843-847, 2010.
- [3] Dennis Y. C. Leung, *et al.* "A review on biodiesel production using catalyzed transesterification", *Applied Energy*, **87**, pp. 1083-1095, 2010.
- [4] Roberto Armenta, *et al.* "Transesterification of Fish Oil to Produce Fatty Acid Ethyl Esters Using Ultrasonic Energy", *Journal of the American Oil Chemists' Society*, **84**, pp. 1045-1052, 2007.
- [5] Ayhan Demirbas. "Comparison of transesterification methods for production of biodiesel from vegetable oils and fats", *Energy Conversion and Management*, **49**, pp. 125-130, 2008.
- [6] N. Akhavan Moghaddam, *et al.* "Trans-Esterification for Production of Biodiesel from Waste Frying Oil (WFO)", *Engineering and Technology*, **71**, pp. 615-619, 2010.
- [7] M. Kim, *et al.* "Transesterification of Glycerides Using a Heterogeneous Resin Catalyst Combined with a Homogeneous Catalyst", *Energy & Fuels*, **22**, pp. 3594-3599, 2008.
- [8] L. Andreani, J. D. Rocha. "Use of ionic liquids in biodiesel production: a review", *Brazilian Journal of Chemical Engineering*, **29**, pp. 1-13, 2012.
- [9] L. Yu. Dolgikh, *et al.* "Influence of ion-exchange and impregnation modification of zeolite X on its catalytic properties in the alkylation of toluene with methanol", *Theoretical and Experimental Chemistry*, **42**, pp. 37-41, 2006.
- [10] Luís Adriano S. do Nascimento, *et al.* "Comparative study between catalysts for esterification prepared from kaolins", *Applied Clay Science*, **51**, pp. 267-273, 2011.
- [11] Soumaya Bouguerra Neji, *et al.* "Esterification of Fatty Acids with Short-Chain Alcohols over Commercial Acid Clays in a Semi-Continuous Reactor", *Energies*, **2**, pp. 1107-1117, 2009.
- [12] Ping Wang, *et al.* "Synthesis of ZSM-5 zeolite from expanded perlite/kaolin and its catalytic performance for FCC naphtha aromatization", *Catalysis Communications*, **8**, pp. 1452-1456, 2007.
- [13] Sathy Chandrasekhar, P. N. Pramada. "Kaolin-based zeolite Y, a precursor for cordierite ceramics", *Applied Clay Science*, **27**, pp. 187-198, 2004.
- [14] S. L. C. Ferreira, *et al.* "Box-Behnken design: An alternative for the optimization of analytical methods", *Analytica Chimica Acta*, **597**, pp. 179-186, 2007.
- [15] Gemma Vicente, *et al.* "Optimisation of integrated biodiesel production. Part I. A study of the biodiesel purity and yield", *Bioresource Technology*, **98**, pp. 1724-1733, 2007.
- [16] Douglas C. Montgomery, *Design and analysis of experiment*, 6th ed. New Jersey: John Wiley & Sons, Inc., 2005.
- [17] Felycia Edi Soetaredjo, *et al.* "KOH/bentonite catalysts for transesterification of palm oil to biodiesel", *Applied Clay Science*, **53**, pp. 341-346, 2011.
- [18] M. Lenarda, *et al.* "Solid acid catalysts from clays: Preparation of mesoporous catalysts by chemical activation of metakaolin under acid conditions", *Journal of Colloid and Interface Science*, **311**, pp. 537-543, 2007.
- [19] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. New York: Wiley, 1978.
- [20] César A. Contreras, *et al.* "Preparation of Sodium Aluminate From Basic Aluminium Sulfate", *The AZO Journal of Materials Online*, **2**, 2006.
- [21] C. A. Ríos, *et al.* "Synthesis of zeolite LTA from thermally treated kaolinite", *Rev. Fac. Ing. Univ. Antioquia*, **53**, pp. 30-41, 2010.
- [22] Treacy M.M.J., Higgins J.B., *Collection of Simulated XRD Powder Patterns for Zeolites*, 2001.