Removal of Free Fatty Acid in Soybean Oil by using $KHSO_4$ Supported on Mordenite Zeolite

Supatra Khabuanchalad[*a], Natkanin Supamathanon[b], Sudarat Sombatsri[b], Jatuporn Wittayakun[c]

[a]Department of Science and Math, Faculty of Agriculture and Technology,
Rajamangala University of Technology Isan, Surin Campus, Surin, 32000, Thailand
[b]Department of Applied Chemistry, Faculty of Sciences and Liberal Arts,
Rajamangala University of Technology Isan, Nakhon Ratchasima, 30000, Thailand
[c]School of Chemistry, Institue of Science, Suranaree University of Technology,
Nakhon Ratchasima, 30000, Thailand
***Corresponding author**: khabuanchalads@gmail.com

Abstract

In this study, the conversion of oleic acid (as a Free Fatty Acid), presented in soybean oil, was investigated by esterification reaction using $KHSO_4$ supported on proton mordenite as a catalyst ($KHSO_4$/H-MOR). The catalyst was characterized by XRD, FTIR, NH_3-TPD and nitrogen adsorption. The reaction condition including catalyst types, catalyst amount, methanol to oil mole ratio, and reaction time were studied to obtain the optimum condition that gives maximum FFA conversion. The FFA conversion was determined using titration method. The study shows that $KHSO_4$/H-MOR catalyst yielded the maximum FFA conversion (99%) for the esterification reaction at 70 °C with 4 h reaction time, methanol to oil mole ratio of 30:1 and 3 wt% catalyst loading.

Keywords: Free Fatty Acids, Esterification, $KHSO_4$, H-MOR, Biodiesel

1. Introduction

Typically, biodiesel is produced by transesterification of triglycerides feedstock with methanol or other short-chained alcohols using homogeneous or heterogeneous catalysts. Triglycerides can be extracted from two sources: vegetable oil such as rapeseed, soybean, sun flower, palm, and corn oils, and from animal fat [1]. The literature suggests that 70-95% of biodiesel prices vary accordingly with the costs of raw materials. Biodiesel feedstock such as waste cooking oil and oils from seeds of non-edible plants has been considered [2] since the price of waste cooking oil is two to three times as cheap as vegetable oil. In addition to its lower price, waste cooking oil requires a lower cost for waste treatment [3]. However, one of the major drawbacks of such feedstock is its high content of free fatty acid (FFA), which consequently causes soap formation with alkaline catalyst. Soap production yields rise to gel formation, increases biodiesel viscosity, and prevents the separation of methyl ester and glycerine. As the result, it is necessary that FFA in the biodiesel feedstocks be reduced prior to biodiesel production with alkali catalyzed transesterification.

Esterification is normally employed to reduce FFAs in oils with homogeneous acid catalyst (such as H_2SO_4 or HCl) which convert FFA to ester. However, the use of homogeneous acid catalyst may bring about some potential problems such as difficulty in separating catalyst and product, which is related to environment and corrosion problems. Therefore, extensive research on the use of heterogeneous acid catalysts has been carried out to overcome the problems stated above.

Zeolites and modified zeolite catalysts can be used as a solid catalyst to reduce FFA via esterification. [4-6] Moderate zeolite is a type of zeolite containing strong acid sites and hydrophobic surface which could be used to catalyze the esterification. For example, the modification of proton-mordenite (H-MOR) with phosphoric acid is an effective heterogeneous acid catalyst for esterification of FFA in neem oil. [6]

In the present study, we used a reactant prepared by mixing oleic acid (represented as FFA) and soybean oil, as a representation of waste cooking oil. The conversion of oleic acid in waste cooking oil over heterogeneous acid catalysts was investigated. The catalyst was prepared by impregnation of potassium bisulphate, an acidic salt used in many organic reactions [7], on proton-mordenite zeolite ($KHSO_4$/H-MOR). The effects of reaction time, methanol to oil mole ratio and amount of catalyst on the conversion of FFA were also examined.

2. Experimental

2.1 Materials

H-Mordenite (HSZ-660-HOA,) (Si/Al = 30) was purchased from Tosoh coporation. Potassiumbisulfate ($KHSO_4$, Ajax), oleic acid ($C_{18}H_{34}O_2$, QREC,), sodium hydroxide (NaOH, QREC), methanol (CH_3OH, Merck), ethanol (C_2H_5OH, QREC) and phenolphthalein are reagent grade.

2.2 Catalyst Preparation

An approximate amount of 3.0 g of H-MOR in 15 ml of distilled water was mixed with 1.5 g of $KHSO_4$. The mixture was subsequently stirred at room temperature for 6 h, then dried at 40 ^{o}C and at 120 ^{o}C, respectively, for 6 h, and finally yielded white powder $KHSO_4$/H-MOR catalyst.

2.3 Catalyst Characterization

Functional groups within the zeolite H-MOR structure were identified by FTIR (Perkin Elmer Spectrum 100) connected with Universal ATR (UATR), using KBr as a medium. The IR spectra were scanned in the range of 4,000 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1} Phase and crystallinity of zeolite H-MOR were confirmed by powder XRD (Bruker AXS diffractometer D5005) with nickel filter Cu K_α radiation scanning from 5 to 50° at a rate of 0.05 °/s with 40 kV and 40 mA. The specific surface areas (BET) of the samples were determined through a nitrogen adsorption isotherm by a Bel-Japan, Bel Sorp mini II gas adsorption analyzer at liquid nitrogen temperature. The sample was degassed at 150 °C for 6 h before the measurement.The acid site of samples was determined using Ammonia-Temperature Programmed Desorption; NH_3-TPD. The samples (100 mg) were then pretreated at 300 °C. After that, $NH_3$was flowed through the samples and purged at 70 °C. The analysis was performed at the temperature of 70-610 °C.

2.4 Preparation of reactant representing waste cooking oil

The reactant representing waste cooking oil was prepared by mixing 80 ml of soybean oil with 20 ml of oleic acid, resulting a reactant with 20%w/w of oleic acid in soybean oil.

2.5 Conversion of FFA in waste cooking oil

Acid catalyzed esterification reaction was carried out in a round-bottomed flask equipped with a reflux condenser. The reaction flask was immersed in a chamber containing water. Waste cooking oil and methanol was mixed in a mole ratio of 1:10 and then added into the round-bottomed flask together with 3 wt% of acid catalyst. The reaction was carried out at 70 ^{o}C for 4 h. The reaction mixture was, then, centrifuged to separate the used catalyst and subsequently evaporated at 60 ^{o}C to remove methanol. The conversion of free fatty acid from the reaction using three different acid catalysts; $KHSO_4$, H-MOR and $KHSO_4$/H-MOR was later compared. The effect of $KHSO_4$/H-MOR amount, methanol to oil molar ratio, reaction time (1 to 5h) and reusability of catalyst were also investigated.

The acid value of the reaction mixture was determined by titration according to the AOAC method [8]. A 5-gram of sample was mixed with 50 ml of ethanol, the solution was then titrated with 0.1 N NaOH by using phenolphthalein as an indicator. The acid value was calculated in term of mgNaOH/gram of oil and was further used to calculate the free fatty acid conversion.

The conversion of FFA (reduction in acid value) was calculated using the equation;

$$\text{FFA conversion (\%)} = \left[\frac{\text{AV}_\text{i} - \text{AV}_\text{f}}{\text{AV}_\text{i}}\right] \times 100$$

Where AV_i is the acid value in the initial reactant and AV_f is the acid value in reaction mixture after esterification reaction.

3. Results and Discussion

3.1 Catalyst Characterization

IR spectroscopy

IR spectroscopy was used to characterize functional group of H-MOR, $KHSO_4$ and $KHSO_4$/H-MOR as shown in figure 1. The spectrum of H-MOR includes a broad band at 3400 cm^{-1} attributed to OH stretching of water and a band at 1088 cm^{-1} as a result of asymmetric stretching modes of Si-O-Si in zeolite H-MOR [9]. The spectrum of $KHSO_4$ showed bands at 1178 cm^{-1} and 886 cm^{-1} attributed to asymmetric stretching and symmetric stretching of SO_4^{2-}, respectively [10]. The spectrum of $KHSO_4$/H-MOR consisted of a band at 1088 cm^{-1} contributed to Si-O-Si in zeolite H-MOR indicating that zeolite structure did not collapse during the catalyst preparation. The peaks at 1178 cm^{-1} and 886 cm^{-1} which belonged to SO_4^{2-} were also observed, indicating the existence of $KHSO_4$ species on catalyst surface.

XRD Spectroscopy

The XRD Patterns of $KHSO_4$/H-MOR along with $KHSO_4$ and H-MOR are displayed in figure 2. The pattern of H-MOR presents characteristic peaks of H-MOR at 2θ = 6.55, 9.78, 13.56, 15.32, 19.74, 22.50, 25.81 and 27.34 respectively [11]. The XRD peaks of H-MOR resemble to the XRD peaks of pristine MOR [12, 13], revealing that the phase of pristine MOR is not changed during the transformation to H-MOR. The XRD pattern of $KHSO_4$/H-MOR includes the characteristic peaks of H-MOR. This evidence suggests that H-MOR structure did not collapse during the catalyst preparation which corresponded to the result from IR spectroscopy which shows the evidence of Si-O-Si in zeolite structure. The peaks attributed to $KHSO_4$ with a weak intensity were also observed, suggesting that the $KHSO_4$ species were presented on the H-MOR surface.

BET Surface Area

Surface Area of zeolite H-MOR and $KHSO_4$/H-MOR were analyzed using Bruner Emmett Teller method as shown in table 1. The surface area of H-MOR was 554.75 m^2/g; however, it was drastically decreased by the deposition of $KHSO_4$. This was assumed to be an effect from the dispersion of $KHSO_4$ over the surface of zeolite H-MOR. Moreover, the decreasing of pore diameter and pore volume of $KHSO_4$/H-MOR relative to those of H-MOR can be implied that some of zeolite pores were blocked by $KHSO_4$ [14].

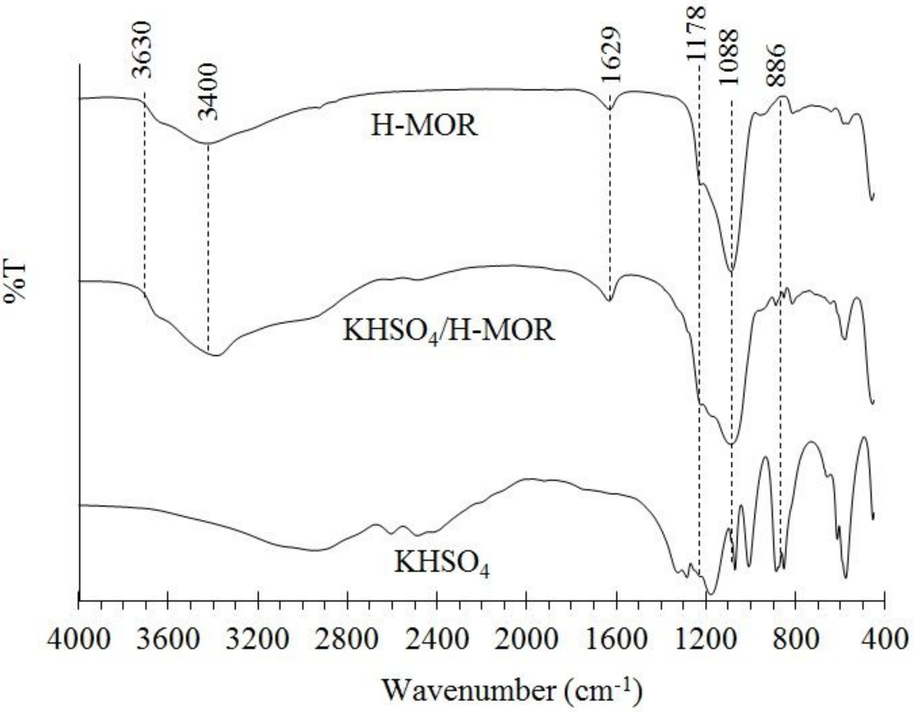

Figure 1. IR Spectra of H-MOR, $KHSO_4$ and $KHSO_4$/H-MOR

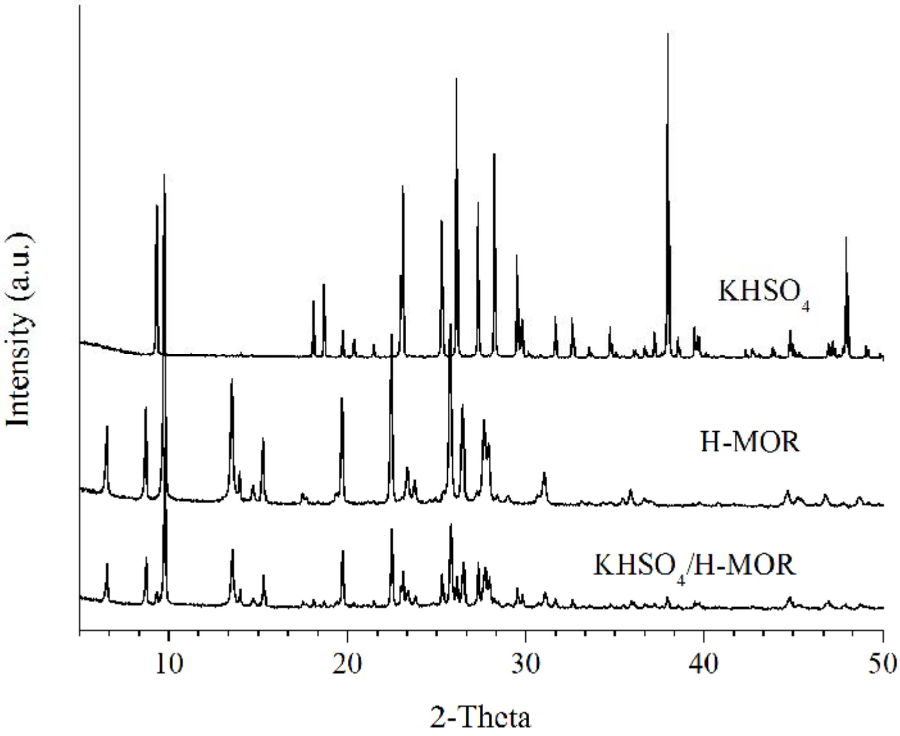

Figure 2. XRD Pattern of $KHSO_4$, H-MOR and $KHSO_4$/H-MOR

Table 1. BET Surface Area of H-MOR and $KHSO_4$/H-MOR

Samples	Surface area (m^2/g)	Mean pore diameter (nm)	Pore volume (cm^3/g)
H-MOR	554.75	2.09	127.46
$KHSO_4$/H-MOR	85.07	1.77	19.545

NH_3 Temperature-Programmed Desorption

Acid amount of H-MOR and $KHSO_4$/H-MOR was determined by means of Ammonia-Temperature-Programmed Desorption as shown in figure 3. TPD profile of H-MOR presents 2 peaks which were well documented for H-MOR [6]. The two peaks of H-MOR in TPD-profile appeared at 100-250 °C and 350-600 °C, which corresponded to weak acid site and strong acid site, respectively [9]. The amount of weak acid and strong acid were 0.752 and 1.163 mmol/g, respectively. Addition of $KHSO_4$ onto H-MOR resulted in the change of TPD profile of H-MOR. The profile showed 5 peaks at 160, 310, 397, 504 and 574 °C with the acid amount 0.316, 0.532, 0.174, 0.443 and 0.222 mmol/g, respectively. These five peaks can be classified into three groups namely; peak at 160 °C attributed to weak acid, peaks at 310 and 397 °C attributed to moderate acid site and peak at 504 and 574 °C attributed to strong acid site. The TPD profile of both samples reveals that depositing of $KHSO_4$ in H-MOR decreases the amount of weak acid site and increased the amount of moderate and strong acid site.

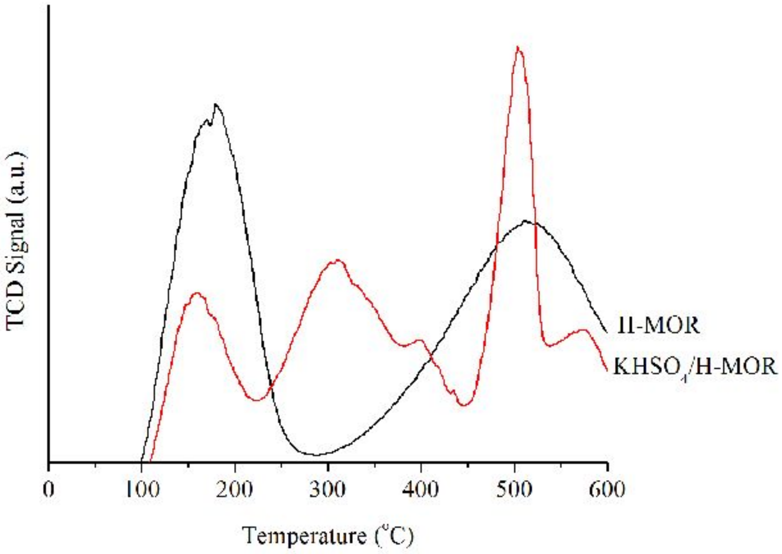

Figure 3. NH_3-TPD profile of H-MOR and $KHSO_4$/H-MOR

Esterification Reaction

Esterification is the reaction that converts fatty acid into ester. In this study, oleic acid was used as a fatty acid in cooking oil. The effect of various reaction parameters such as amount of $KHSO_4$ on catalyst, reaction time, catalyst amount, and methanol:oil mole ratio were studies to optimize the condition for maximum conversion.

Effect of Catalysts

The influence of catalysts on the conversion of oleic acid was investigated using three catalysts: $KHSO_4$, H-MOR and $KHSO_4$/H-MOR. The esterification reaction was carried out at 70 °C using the catalysts with 3 wt% reactant, methanol: oil mole ratio at 30:1, and 4 h reaction time. The esterification over $KHSO_4$ was performed under 1 h reaction time, which is the optimum reaction time for $KHSO_4$. As shown in table 2, the conversion of oleic acid over H-MOR was as low as 13.56% whereas the conversion of oleic acid over $KHSO_4$ and $KHSO_4$/H-MOR were 97.97% and 99.02%, respectively. These results were related to the acid property of catalyst as shown in the NH_3-TPD results. Since esterification reaction requires an acid catalyst [15], deposition of $KHSO_4$ on H-MOR increased the acid strength of catalyst which consequently increased the conversion of oleic acid. The conversion of oleic acid over $KHSO_4$ and $KHSO_4$/H-MOR were not significantly different. However, we selected $KHSO_4$/H-MOR as a suitable catalyst for esterification reaction since $KHSO_4$ can be dissolved in an aqueous solution which causes difficulty in catalyst reutilization.

Table 2. Conversion of oleic acid over $KHSO_4$, H-MOR and $KHSO_4$/H-MOR

Catalysts	Acid value in the initial reactant (mgNaOH/gram of oil)	Acid value in reaction mixture after esterification (mgNaOH/gram of oil)	FFA Conversion (%)
$KHSO_4$	28.54	0.58	97.97
H-MOR	28.54	6.12	13.56
$KHSO_4$/H-MOR	28.54	0.28	99.02

Reaction condition: catalyst amount = 3 wt%, methanol: oil mole ratio = 30:1, and temperature = 70 °C, reaction time = 4 h

Effect of reaction time

Typically, activity of reaction with heterogeneous catalyst increases simulteneously with reaction time until it reaches equilibrium [16]. In order to calculate the time taken to reach equilibrium state, the esterification reaction with 1, 2, 3, 4 and 5 h reaction times were investigated. The results, as shown in figure 4, indicate that as the reaction time increases from 1 h to 2 h and 3 h, the oleic acid conversion is substaintially increased from 52.14% to 72.04% and 90.26%, respectively, whereas increasing reaction time to 4 and 5 h, slightly increases the oleic conversion. These results reveal that the esterification reaction of oleic acid on $KHSO_4$/HMOR requires 4 h reaction time to reach equilibrium state. After the equilibrium state, the oleic conversion is almost unchanged which corresponds to the study of Jeenpadiphat and Tungasmita [14]. Hence the reaction time at 4 h was used for further study.

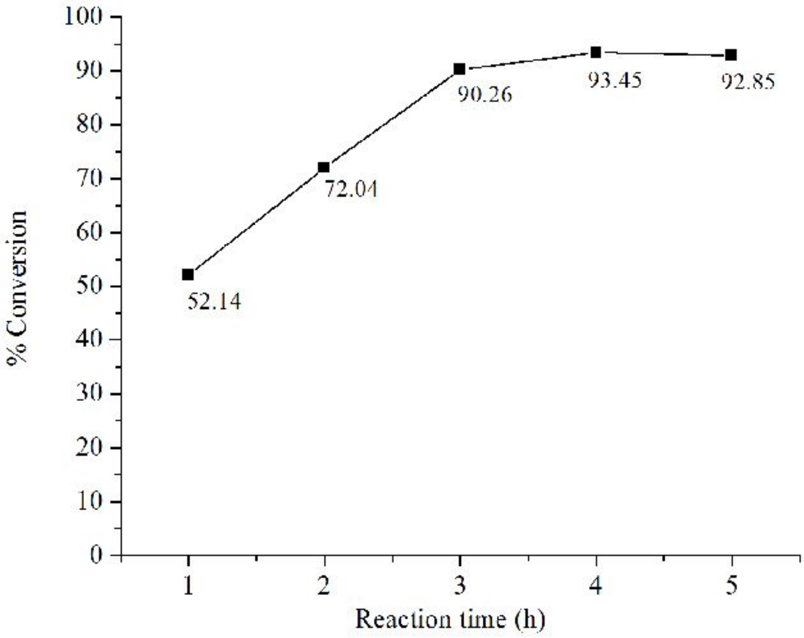

Figure 4. Conversions of oleic acid at different reaction time, Reaction condition: catalyst amount = 3 wt%, methanol to oil mole ratio = 10:1, and temperature = 70 °C

Effect of catalyst amount

The effect of catalyst amount on oleic acid conversion was investigated by varying the catalysts amount from 1-5 wt% of reactant used. As shown in figure 5, the oleic conversion increases from 81.43% to 91.59% as catalyst amount increased from 1 to 2 wt%. However, when the catalyst amount was increased to 3 wt% and 4 wt%, the conversion slightly rises to 93.45% and 93.94%, respectively. The oleic acid conversion reaches a maximum at 93.69% at 5 wt% catalyst amount. It is remarkable that at the reaction with 1 wt% catalyst, the conversion was low because there was not enough active site for reactant in the catalytic process. When the amount of catalyst increased, the oleic conversion also increased, corresponding to the study by He *et al.* [17]. When the amount of catalyst exceeded 3 wt%, the conversion did not increase in accordance with that of the catalyst as there are enough active sites for the reactant. As a result, the reaction with 3 wt% catalyst will be used for further study.

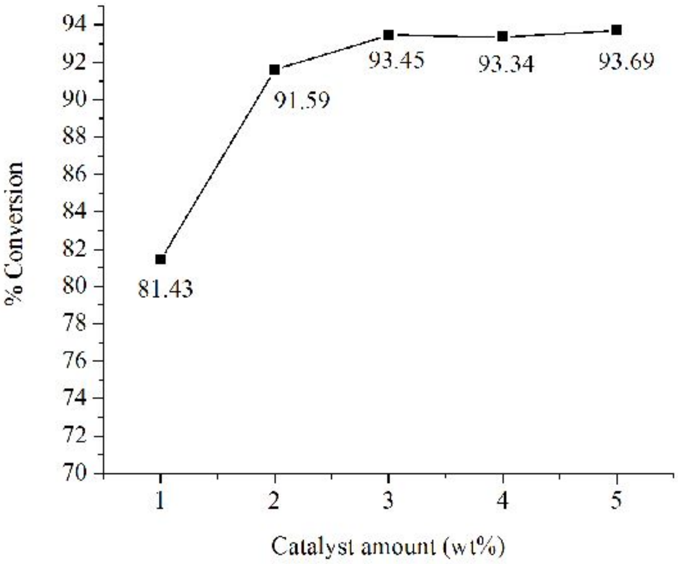

Figure 5. Effect of catalyst amount on conversion of oleic acid, Reaction condition: methanol to oil mole ratio = 10:1, reaction time = 4 h and temperature = 70 °C

Effect of methanol/oil mole ratio

The methanol to oil mole ratio is one of the most essential parameters that effect the oleic acid conversion. To investigate the effect of methanol to oil mole ratio, the esterification reaction was carried out by means of varying the ratio of methanol to oil at 5:1, 10:1, 20:1, 30:1, and 40:1, respectively. As shown in figure 6, the conversion of oleic acid increases with increasing methanol to oil mole ratio. The change of mole ratio from 5:1 to 10:1 showed a remarkably increase in oleic acid conversion (from 52.14% to 93.45%); however, raising the methanol to oil mole ratio from 20:1 to 30:1 and 40:1 slightly increases the conversion of oleic acid to 96.14%, 99.02% and 99.26%, respectively.

Since the esterification of oleic acid is an equilibrium-limited reaction, to increase the product, the reaction is generally carried out by taking methanol in excess in order to enhance the forward reaction [18]. The results from the present study correlate with the study of Kusmiyati and Agung Sugiharto [19], which found that the conversion of oleic acid rise with the increase of methanol: oil mole ratio.

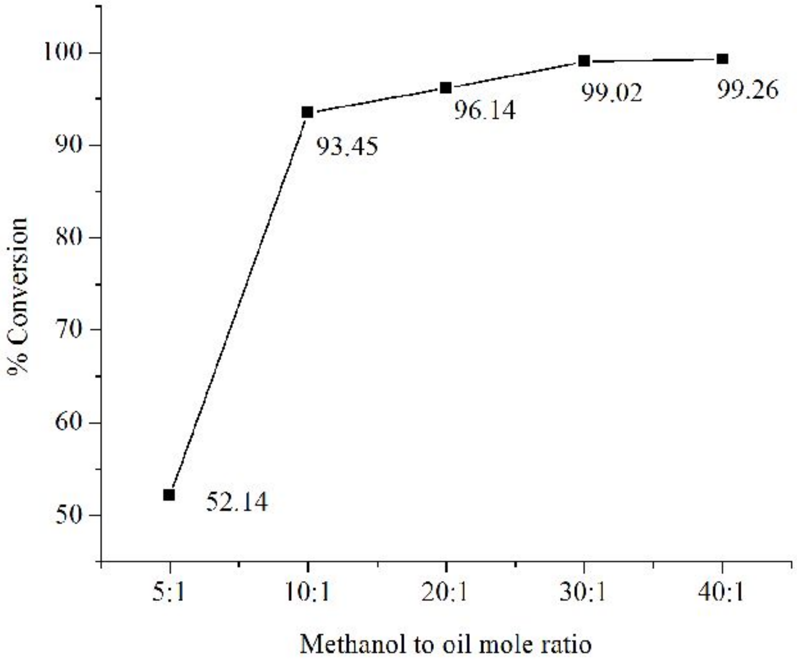

Figure 6. Effect of methanol/oil mole ratio on conversion of oleic acid, Reaction condition; catalyst amount = 3 wt%, reaction time = 4 h and temperature = 70 °C

From the above result, the ratio of methanol: oil at 30:1 and 40:1 yielded almost the same oleic acid conversion i.e. 99.02% and 99.26%, respectively. Thus, the methanol: oil mole ratio at 30:1 was selected for further study.

According to the aforementioned results, the optimum conditions for esterification of oleic acid in soybean oil are follows: catalyst: $KHSO_4$/H-MOR, mole ratio of methanol to oil 30:1, 4 h reaction time, reaction temperature 70 ^oC and catalyst amount 3 wt.%.

Table 3 reports literatures on esterification reaction of oleic acid with methanol over different catalysts. It was found that the oleic conversion over $KHSO_4$/H-MOR is higher than that over SO_4^{2-}/SnO_2 [20], phosphonium-based deep eutectic solvent *(DES)* [21], niobic acid [22] and sulfuric acid [23]. The oleic conversion obtained from this work is comparable with the oleic conversion over TDA-PTA [24] and SO_3H-functionalized ionic liquid [25]. However, reaction temperature and time period taken for the esterification over TDA-PTA and SO_3H-functionalized ionic liquid were relatively higher than those from this work. Obviously, the catalytic performance of $KHSO_4$/H-MOR is comparable to those of the reported catalysts.

Table 3. Esterification of oleic acid with methanol over different catalysts

Catalysts	Alcohol to oleic acid mole ratio	Temperature (°C)	Time (h)	Oleic acid conversion (%)	References
SO_4^{2-}/SnO_2	10:1	80	4	50	[20]
Phosphonium-based deep eutectic solvent (DES)	6:1	150	30 min	95	[21]
Niobic acid	6:1	250	Continuous esterification	90	[22]
Sulfuric acid	60:1	60	2	92.30	[23]
TDA-PTA	8:1	80	6	99.5	[24]
SO_3H-functionalized ionic liquid	10:1	80	12	99.5	[25]
$KHSO_4$/H-MOR	10:1	70	4	93.45	This work
$KHSO_4$/H-MOR	30:1	70	4	99.02	This work

Catalyst reutilization

To conduct the catalyst reutilization test, after each use, catalyst was recycled by centrifugation, washing thoroughly with hexane and drying at 150 °C before the next use. The conversion of oleic acid over esterification in four consecutive experiments was tested as shown in figure 7. The reutilization test showed a slightly decrease in oleic acid conversion for catalyst in the second use. The conversion is reduced from 99.02% for fresh catalyst, to 84.27% for the first reuse catalyst. However, the conversion significantly decreases after the third (6.91%) and the fourth use (3.92%). The reduction in catalytic activity may involve two consequences. First, there is a partial leaching of $KHSO_4$ from the H-MOR support, resulting in the loss of active sites. Second, the number of acid sites remaining on the catalyst is lower after the reaction, probably due to the interaction of acid group with methanol [26]. To confirm this hypothesis, the analysis of used catalysts has been done using thermogravimetric analysis as shown in figure 8. Weight loss of H-MOR and $KHSO_4$/H-MOR was found to be 8% and 17%, respectively. The percentage of weight loss of $KHSO_4$/H-MOR is higher than that of H-MOR because of the loss of $KHSO_4$ on the surface of H-MOR.

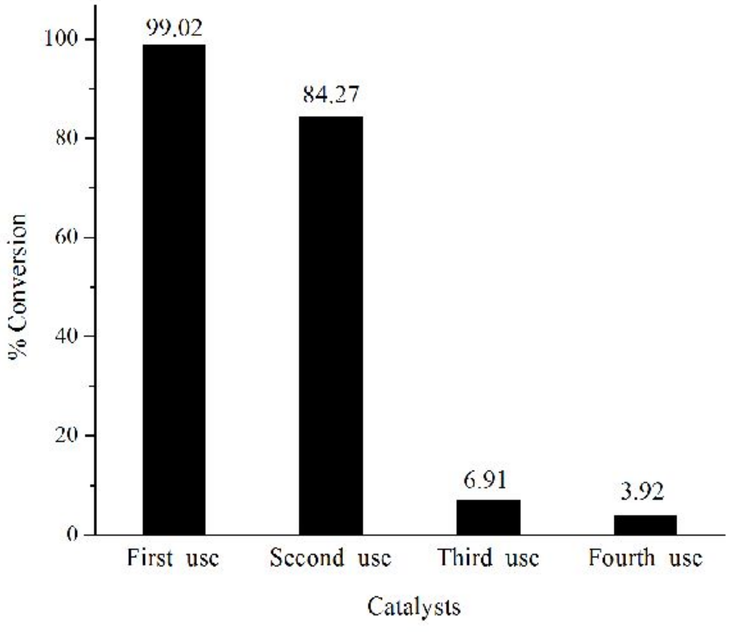

Figure 7. Reusability performance of $KHSO_4$/H-MOR

The thermogram of catalysts after the first and second use showed weight loss below 270 ^{o}C which is attributed to mainly methanol. Moreover, they also show evidence of weight loss at 270-550 ^{o}C which caused by the loss of adsorbed fatty acids [6]. The weight loss according to adsorbed fatty acids is 15% and 30% for catalysts after the first and second use, respectively. The presence of methanol and free fatty acid confirms that the catalyst was deactivated due to the adsorption of reactant on catalyst surface which consequently block the active site of catalyst surface. Thus, the more frequency catalysts being used, the more reactants being adsorbed on its surface.

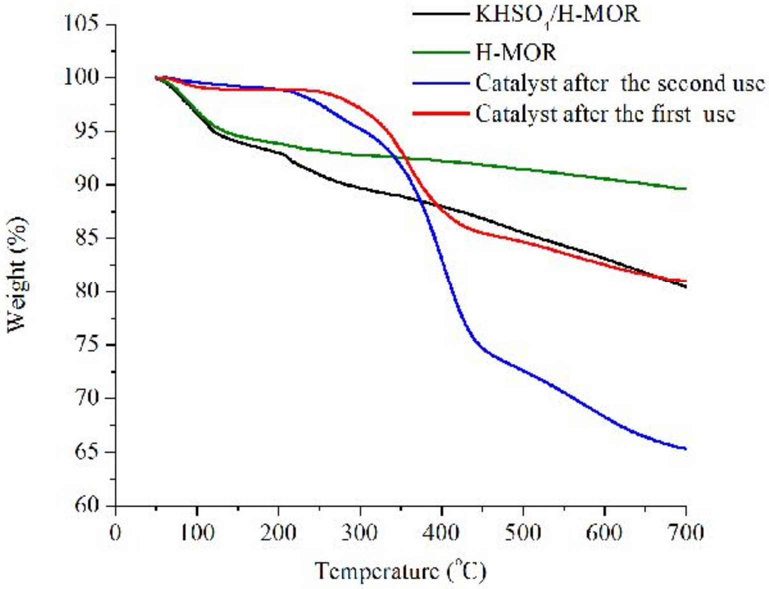

Figure 8. Thermogravimetric analysis of the used catalysts compared to the fresh catalyst

4. Conclusions

$KHSO_4$/H-MOR is an effective catalyst for esterification, yielding a high oleic conversion of 99.02%, among the tested catalysts. Since esterification reaction required an acid catalyst, depositing $KHSO_4$ on H-MOR increased the amount of acid site of catalyst as shown by NH_3-TPD results. The mole ratio of methanol: oil of 30:1, 4 h reaction time, 70 ^{o}C reaction temperature, and 3 wt% catalyst amount were suggested as the optimum conditions for esterification of free fatty acid. The catalyst reutilization showed that the conversion over $KHSO_4$/H-MOR drastically decreased after the second use. This was assumed to be a result of the leaching of $KHSO_4$ from H-MOR, or the loss of acid site due to the interaction of acid group with methanol.

Acknowledgement

This work was supported financially by National Research Council of Thailand (NRCT).

References

[1] Einloft, S., Magalhães, T. O., Donato, A., Dullius, J., Ligabue, R. (2008). Biodiesel from Rice Bran Oil: Transesterification by Tin Compounds. **Energy&Fuels**, 22: 671-674.

[2] Ullah, Z., Bustam, M. A., Man, Z. (2015) Biodiesel production from waste cooking oil by acidic ionic liquid as a catalyst. **Renew Energ**, 77: 521-526.

[3] Kiakalaieh, A. T., Amin, A. S., Mazaheri, H. (2013). A review on novel processes of biodiesel production from waste cooking oil. **Appl Energ**, 104: 683-710.

[4] Chung, K. H., Park, B.G. (2009). Esterification of Oleic Acid in Soybean Oil on Zeolite Catalysts with Different Acidity. **J. Ind. Eng. Chem**., 15: 388-392.

[5] Chung, K.H., Changet, D. R., Park, B. G. (2008). Removal of free fatty acid in waste frying oil by esterification with methanol on zeolite catalysts. **Bioresour. Technol.**, 99: 7438-7443.

[6] Sathya Selvabala,V., Varathachary, T. K., Selvaraj, D. K., Ponnusamy,D. K., Subramanian, S. (2010). Removal of free fatty acid in Azadirachtaindica (Neem) seed oil using phosphoric acid modified mordenite for biodiesel production. **Bioresour. Technol.,** 101: 5897-5902.

[7] Baghernejad, B. (2012). Potassium hydrogen sulfate: An efficient catalyst in organic reactions**. Eurjchem.**, 3(1): 125-128.

[8] Association of Official Analytical Chemists. (2000). Official Methods of Analysis. 17th ed., Washington DC.

[9] Intarapong, P.,Iangthanarat, S., Phanthong, P., Luengnaruemitchai, A., Jai-In, S. (2013). Activity and basic properties of KOH/mordenite for transesterification of palm oil.**J Energy Chem**., 22: 690-700.

[10] Periasamy, A., Muruganand, S., Palaniswamy, M. (2009). Vibrational Studies of Na_2SO_4, K_2SO_4, $NaHSO_4$, and $KHSO_4$ Crystals. **Rasayan J. Chem.**, 2(4): 981-989.

[11] Kulawong, S., Prayoonpokarach, S., Roessner, F., Wittayakun, J. (2015). Acidity of Modifired Mordenites Synthesized from Rice Husk Silica and Catalytic Transformation of Methylbutynol. **Quim Nova**., 38(2): 191-195.

[12] Kim, G. J. and Ahn, W. S. (1991). Direct synthesis and characterization of high-SiO_2-content mordenites. **Zeolite.**, 11(7), 745-750.

[13] Mao, Y., Zhou, Y., Wen, H., Xie, J., Zhang, W., and Wang, J. (2014) Morphology-controlled synthesis of large mordenite crystals. **New J. Chem**., 38, 3295-3301.

[14] Kubička, D., Kumar, N., Venä1äinen, T., Karhu, H., Kubičková, I., Österholm, H., Murzin, D. Y. (2006). Metal−Support Interactions in Zeolite-Supported Noble Metals: Influence of Metal Crystallites on the Support Acidity. **J. Phys. Chem. B.**, 110(10), 4937-4946.

[15] Shanmugam, S., Viswanathan, B., Varadarajan. T. K. (2004). Esterification by solid acid catalysts - a comparison. **J MolCatal A-Chem.**,223(1): 143-147.

[16] 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.

[17] He, L., Qin, S., Chang, T., Gao, X. (2013). Biodiesel synthesis from the esterification of free fatty acids and alcohol catalyzed by long-chain Brønsted acid ionic liquid. **Catal Sci Technol**., 3(4): 1102-1107.

[18] Brahmkhatri, V. and Patel, A. (2011). Biodiesel Production by Esterification of Free Fatty Acids over 12-Tungstophosphoric Acid Anchored to MCM-41. **Ind. Eng. Chem. Res**., 50: 6620-6628.

[19] Kusmiyati, K. and Sugiharto, A. (2010). Production of Biodiesel from Oleic Acid and Methanol by Reactive Distillation. **Bulletin of Chemical Reaction Engineering & Catalysis**, 5 (1): 1- 6.

[20] Moreno, J.I., Jaimes, R., Gómez, R., and Gómez, M. (2011) Evaluation of sulfated tin oxides in the esterification reaction of free fatty acids. **Catal Today**, 172(1): 34-40.

[21] Williumson, S.T., Shahbaz, K., Mjalli, F.S., AlNashef, I. M. and Farid, M.M. (2017) Application of deep eutectic solvents as catalysts for the esterification of oleic acid with glycerol. **Renew energ**, 114: 480-488.

[22] Rade, L.L., Lemos, C., Barrozo, M.A.S., Ribas, R.M., Monterio, R.S. and Hori, C.E. (2018) Optimization of continuous esterification of oleic acid with ethanol over niobic acid. **Renew energ**, 115: 208-216.

[23] Berrios, M, Siles, J., Martín, M.A. and Martín, A. (2007) A kinetic study of esterification of free fatty acids (FFA) in sunflower oil. **Fuel**, 86: 2383-2388.

[24] Wang, H.H., Liu, L.J. and Gong S.W. (2017) Esterification of oleic acid to biodiesel over a 12-phosphotungstic acid-based solid catalyst. **J Fuel Chem Technol**, 45(3): 303-310.

[25] Zhou, S., Liu, L., Wang, B., Xu, F., and Sun, R. (2013) Facile biodiesel synthesis from esterification of free fatty acid catalyzed by SO_3H-Functionalized Ionic Liquid. **Asian J. Chem.**, 25(1): 240-244.

[26] Melero, J. A., Bautista, L. F., Morales, G., Iglesias, J., Briones, D. (2009). Biodiesel production with heterogeneous sulfonic acid-functionalized mesostructured catalysts. **Energy & Fuels**, 23: 539-547.