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Original Research Article

Kanemite: an easily prepared and highly efficient catalyst for biodiesel production optimized by response surface methodology

Abolfazl Ghaffari, Mahdi Behzad*

Department of chemistry, Semnan University, Semnan 35351-19111, Iran

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ABSTRACT

Kanemite was readily prepared and used as solid base catalyst for transesterification of sunflower oil to fatty acid methyl ester (FAME). The catalyst was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), N₂ adsorption-desorption and field emission scanning electron microscopy (FESEM) techniques. Central Composite Design (CCD) coupled with Response Surface Methodology (RSM) was utilized to study the effects of the system variables such as catalyst amount, methanol to oil molar ratio, reaction time and specifically, the effect of interaction between process variables on the conversion of oil to biodiesel. Under the optimum reaction conditions (5 wt.% catalyst loading, methanol to oil molar ratio 22:1 and reaction time 240 min), the highest predicted and experimental fatty acid methyl ester conversions were 95.97% and 94.17%, respectively. Besides, the reusability of the prepared catalyst was checked for five cycles under the optimal reaction conditions. No significant loss of the product yield was observed.

Keywords: Biodiesel; Kanemite; Transesterification; Solid base catalyst; Response surface methodology.

Introduction

Fossil energy resources are limited, and their use has many disadvantages including ecological contaminations. In this regard, the use of green fuels as a replacement of such resources has drawn great attention [1-3]. Biofuels are clean, renewable, biodegradable and non-toxic fuels which are conventionally produced through transesterification of refined vegetable oils with methanol. Synthetic biodiesel is usually methyl ester of long chain fatty acids. Homogeneous base catalysts, such as sodium hydroxide and potassium hydroxide are normally used to synthesize biodiesel. The major drawback of such homogeneous catalysis is the difficulty of the removal of the catalysts [4, 5]. To overcome this problem, heterogeneous catalysts are being developed for biodiesel production, indeed, such catalysts are getting great attention in many other chemical industries. Heterogeneous catalysts can be easily separated by filtration. They can be reused and recycled several times. Besides, they do not require additional neutralization processes. They can also produce a high purity glycerol by-product. Heterogeneous catalysts have their own drawbacks, e.g., severe reaction conditions such as high reaction temperatures, long reaction times and moisture sensitivity [6, 7]. Various heterogeneous acid and base catalysts have been developed and used for biodiesel production, and among them, basic catalysts have shown higher activity [8-12]. Once again and unfortunately, this higher activity is compensated by some key limitations. One of the most important disadvantages of the above mentioned catalysts, from an industrial point of view, is rapid poisoning of their surface active sites upon exposing to ambient air due to chemisorption of CO₂ and H₂O. For example, CaO chemisorbs significant amount of carbon dioxide and water in a few minutes and gets poisoned. Previous studies have shown that sodium silicates were highly-active and recyclable with little deactivation upon exposure to air [13-16].

Kanemite (NaHSi₂O₅·3H₂O) is a layered material which is composed of single layered silicate sheets of linked SiO₄ tetrahedra with hydrated Na ions in the interlayers. Kanemite was discovered as a natural mineral in Lake Chad by Johan and Maglione in 1972 and its chemical synthesis was reported by Beneke and Lagaly [17, 18]. Kanemite exhibits some interesting properties such as high charge density (higher than many clays) and potential application as a catalyst [19].

In this study, kanemite was prepared by a facile procedure. The synthesized sample was characterized and successfully used as a basic heterogeneous catalyst for transesterification of sunflower oil. High catalytic activity was achieved at optimized reaction conditions. The optimization of the experimental factors including catalyst dosage, methanol to oil molar ratio and reaction time on the biodiesel conversion was achieved by Central Composite Design (CCD) coupled with Response Surface Methodology (RSM). At the optimized conditions, high yields of biodiesel production were obtained. The catalyst was also used for five cycles without considerable loss of reactivity.

Experimental

Materials

Commercial edible sunflower oil was obtained from local grocery store. Methanol, sodium hydroxide, silicon dioxide and n-heptane were purchased from Merck chemical company. Methyl heptadecanoate as the standard of GC was purchased from Sigma-Aldrich. All chemical materials were used without further purification.

Catalyst preparation

Kanemite was prepared by a slight modification to the method reported by Beneke and Lagaly [18]. In a typical experiment, 0.2 mol SiO_2 was dispersed in 30 mL of methanol. Cold NaOH solution (0.2 mol NaOH in 7 mL H_2O) was slowly added and the mixture was stirred for 5 h. The resulting slurry was dried at 100 °C for 24 h, and calcined at 700 °C for 60 min. After cooling to room temperature, the obtained solid ($\delta\text{-Na}_2\text{Si}_2\text{O}_5$) was ground and dispersed in 20 times its weight of deionized water and stirred for 30 min. The resulting kanemite was collected by filtration, washed with deionized water and dried at room temperature.

Catalyst characterization

The X-ray diffraction (XRD) patterns were obtained using a Philips X-ray diffractometer (model D8 Bruker) with Cu $K\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). Morphological characterization was performed by scanning electron microscopy (SEM, TESCAN MIRA 3). Textural analysis

was carried out with a BELSORP mini apparatus by determining the nitrogen adsorption/desorption isotherms at -196 °C. Prior to the measurement, the samples were outgassed for 3h at 300 °C. The specific surface area was determined by the BET method. The total pore volume and the pore size distribution (BJH method) were also assessed. FTIR spectra of the samples were collected on a Bruker FT-IR instrument using KBr pellet technique in the range of 4000-400 cm⁻¹.

The transesterification reaction procedure

Transesterification reactions were done in a 50 mL round bottom flask equipped with a reflux condenser. Kanemite was dispersed in the desired amount of methanol with magnetic stirring. Sunflower oil was then added and the mixture was refluxed for the designed time. After the reaction, the catalyst was separated by filtration and then methanol recovered by rotary evaporator at 60 °C. At last, the biodiesel and glycerol were separated within a separation funnel.

The FAME content of the prepared biodiesel sample was quantified by GC-17A Shimadzu gas chromatography equipped with a BP10 capillary column (25 m × 0.32 mm; phase thickness: 0.5 μm) and FID detector according to the standard test methods EN 14103. Methyl heptadecanoate was used as the internal standard. The conversion of the produced biodiesel was calculated with the following Eq. (1):

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

Where $\sum A$ is the total peak area of sunflower oil methyl esters, A_{IS} is the peak area of internal standard, C_{IS} is the concentration of the internal standard solution, V_{IS} is the volume of the internal standard solution and m is the mass of sample [20].

Experimental design and optimization by RSM

Design Expert software, version 7.0.0 was used to optimize the reaction variables. A three-factor-three-level central composite design coupled with response surface methodology was used to investigate the operating conditions of transesterification to obtain a high conversion to biodiesel. The experimental ranges and levels of the variables are listed in Table 1. The studied factors were catalyst amount, methanol to oil molar ratio and reaction time. A

preliminary study was carried out to investigate the level of each factor. The CCD arrangement for experimental design, the results of the tests (conversion %) and their estimated are shown in Table 2.

Table 1. Range of changes and the level of variables in the experimental design.

Independent variables	Symbol	Units	Range and levels		
			-1	0	+1
Catalyst dosage	X ₁	wt. %	3	4	5
Methanol to oil Ratio	X ₂	mol/mol	18	24	30
Reaction time	X ₃	min	120	180	240

Table 2. Experimental design matrix and their responses

Run	X ₁	X ₂	X ₃	Conversion to biodiesel (%)	
				Observed	Predicted
				1	2
2	5	30	120	77.05	79.45
3	5	30	240	94.39	98.35
4	4	24	180	88.32	86.93
5	4	12	180	46.65	49.18
6	3	30	120	86.64	87.05
7	3	30	240	94.63	95.61

8	4	24	180	87.06	86.93
9	3	18	120	55.73	52.67
10	5	18	120	67.37	67.29
11	4	24	180	85.73	86.93
12	5	18	240	88.93	89.42
13	4	24	180	85.86	86.93
14	4	24	300	98.14	96.63
15	4	24	180	85.21	86.93
16	6	24	180	89.71	86.78
17	4	24	180	90.28	86.93
18	4	24	60	65.33	65.94
19	4	36	180	95.92	92.49
20	3	18	240	65.97	64.46

Results and discussion

Catalyst characterization

The XRD patterns of the parent δ - $\text{Na}_2\text{Si}_2\text{O}_5$ (JCPDS: 22-1396) and the kanemite (JCPDS: 25-1309) is shown in Figure 1. The δ - $\text{Na}_2\text{Si}_2\text{O}_5$ contains small amount of α phase impurity (JCPDS: 22-1397). The product obtained after hydration (Kanemite) did not show any reflections assignable to the δ - or α - $\text{Na}_2\text{Si}_2\text{O}_5$ and the XRD pattern is dominated by characteristic peaks of hydrated silicate kanemite. The peak at $2\theta = 8.6^\circ$ is assigned to the (020) reflection and indicates basal spacing ($d = 1.026$ nm). This value is in good agreement with the basal spacing 1.03 nm reported by Johan and Maglione [19, 21].

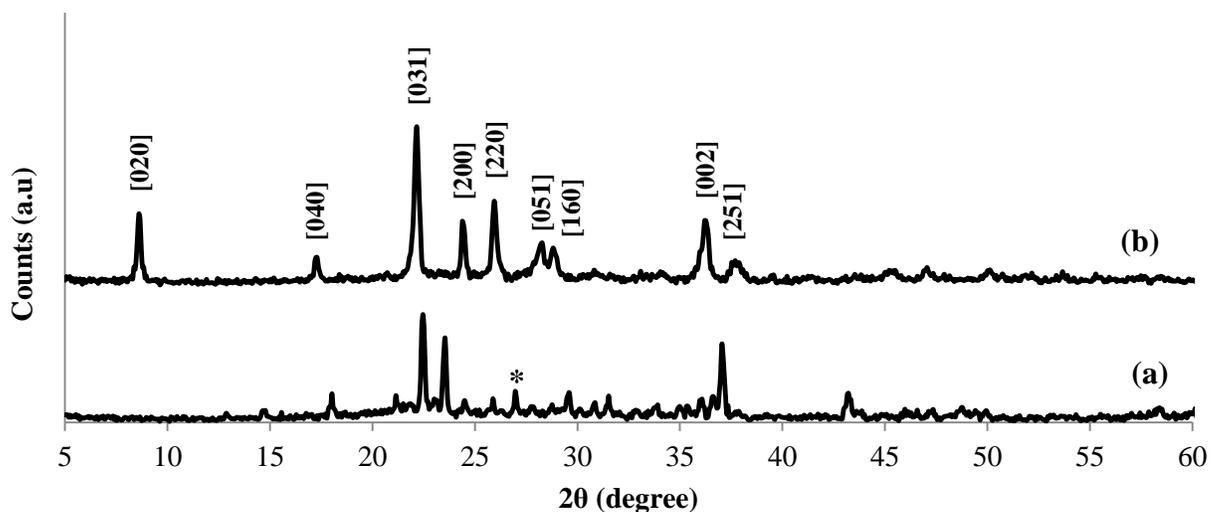


Figure 1. X-ray powder diffraction patterns of: (a) δ - $\text{Na}_2\text{Si}_2\text{O}_5$ and (b) kanemite. * = α - $\text{Na}_2\text{Si}_2\text{O}_5$.

FESEM images of δ - $\text{Na}_2\text{Si}_2\text{O}_5$ and kanemite are shown in Figure 2. The FESEM observations indicated that the morphology of both δ - $\text{Na}_2\text{Si}_2\text{O}_5$ and kanemite were lamellar but the structure of the synthesized δ - $\text{Na}_2\text{Si}_2\text{O}_5$ was a dense arrangement of uniform nanoparticles with roughly spherical shape and the particle diameter size was about 16-40 nm.

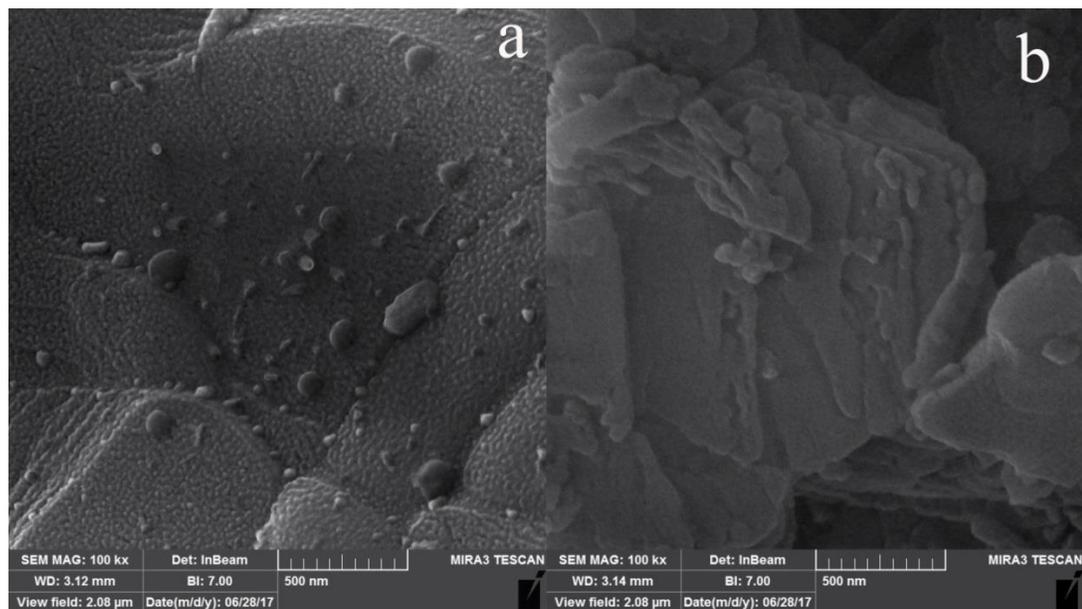


Figure 2. SEM images of the (a) δ - $\text{Na}_2\text{Si}_2\text{O}_5$ and (b) kanemite.

Table 3 shows BET surface area and porosity characteristics of δ - $\text{Na}_2\text{Si}_2\text{O}_5$ and kanemite samples measured by N_2 gas physisorption. The results clearly show that the BET surface area and total pore-volume of kanemite was considerably higher than that of δ - $\text{Na}_2\text{Si}_2\text{O}_5$. The difference in the textural properties of the two samples could be due to the difference in basal spacing measured by X-ray diffraction. The interlayer spacing of silicate sheets contributes to the large specific surface area of the kanemite.

Table 3. BET surface area and porosity characteristics of δ - $\text{Na}_2\text{Si}_2\text{O}_5$ and kanemite

Sample	S_{BET} (m^2g^{-1})	Pore volume (cm^3g^{-1})	V_{mic} (cm^3g^{-1})
δ - $\text{Na}_2\text{Si}_2\text{O}_5$	2.7382	0.0054481	0.6291
kanemite	16.976	0.1611	3.9003

The IR spectra of kanemite and δ - $\text{Na}_2\text{Si}_2\text{O}_5$ are similar to some extent. The main difference is in the 3700-3000 region. In the IR spectrum of kanemite, the two signals, a sharp one at higher wave number (3582 cm^{-1}) and the other broad one at lower wave number (3463 cm^{-1}) were assigned to OH stretching vibrations. The higher frequency narrow band was assignable to the isolated surface OH groups, and the low frequency broad band is due to OH groups involved in interlayer hydrogen bonding. The bands in the range of 1300 and 950 cm^{-1} could be attributed as the asymmetric Si-O-Si and terminal Si-O⁻ stretching vibrations in both structures. Similarly, the bands at 900 and 460 cm^{-1} are due to the symmetric stretching vibrations of (Si-O-Si) bridges. The bands below 460 cm^{-1} are also due to the silicon-oxygen bending and torsional vibration, and the stretching vibrations arising from (Na-O). The FTIR spectra of δ - $\text{Na}_2\text{Si}_2\text{O}_5$ and kanemite are shown in Figure 3. The band at 1167 cm^{-1} indicates that kanemite contains Si-O-Si linkages with a bond angle near 180° [22, 23].

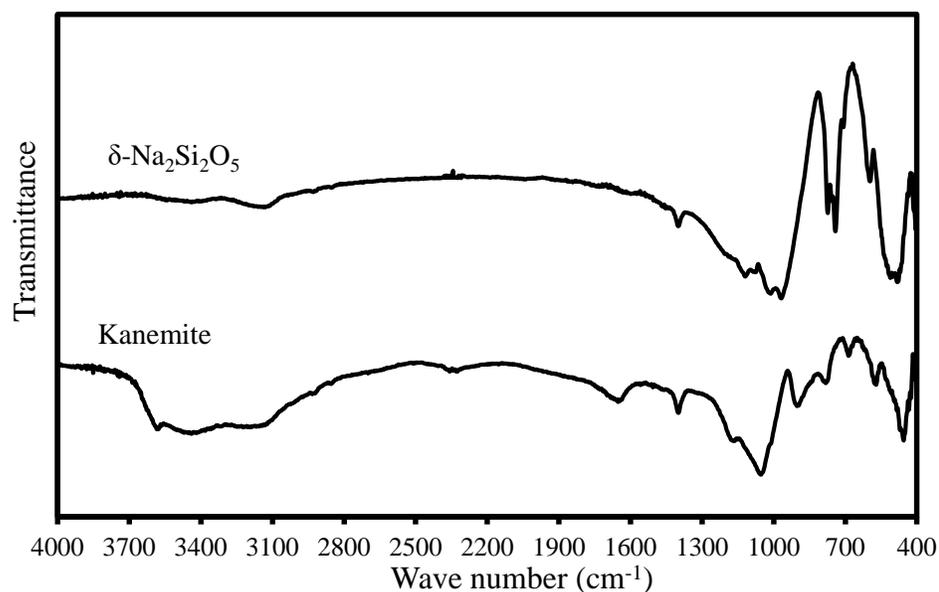


Figure 3. FT-IR spectra of the δ - $\text{Na}_2\text{Si}_2\text{O}_5$ and kanemite.

Statistical analysis

Regression constants and coefficients were obtained from response surface methodology. The quadratic model was obtained from the method of least squares of error for conversion in terms of coded factors which is presented in Eq. (2) as follows:

$$Y = +86.93 + 4.34X_1 + 10.83X_2 + 7.67X_3 - 5.55X_1X_2 + 2.58X_1X_3 - 0.81X_2X_3 - 2.21X_1^2 - 4.02X_2^2 - 1.41X_3^2 \quad (2)$$

Where Y is the biodiesel conversion percent and X_1 , X_2 and X_3 are catalyst amount, methanol to oil molar ratio and reaction time, respectively.

Analysis of variance (ANOVA) was conducted to evaluate the statistical significance of the model equation and result is summarized in Table 4. The model F-value of 49.74 and p-value < 0.0001 showed that the model was statistically significant at 95 percent confidence interval ($p < 0.05$). The p-value probability of lack of fit was greater than 0.05, which confirmed the models significance. Besides, the coefficient of determination (the R-Squared, adjusted-R-Squared) was evaluated to test the model fitness. Close values of R^2 to one and high proximity to the adjusted-R-Squared value showed the high potential of the fitted models. In this work, the values for R-Squared and adjusted-R-Squared were 0.9782 and 0.9585,

receptively. These results indicated that the proposed empirical model is significant and correctly explain the behavior of the response in the experimental domain.

Table 4. Analysis of variance (ANOVA) for quadratic model

Source	Sum of Squares	Degree of freedom (Df)	Mean Square	F Value	p-value Prob > F
Model	3881.332	9	431.2591	49.74226	< 0.0001
X ₁	301.1093	1	301.1093	34.73053	0.0002
X ₂	1875.973	1	1875.973	216.3783	< 0.0001
X ₃	941.7227	1	941.7227	108.6201	< 0.0001
X ₁ X ₂	246.7531	1	246.7531	28.46098	0.0003
X ₁ X ₃	53.40611	1	53.40611	6.159965	0.0324
X ₂ X ₃	5.232612	1	5.232612	0.60354	0.4552
X ₁ ²	122.4091	1	122.4091	14.1189	0.0037
X ₂ ²	406.8701	1	406.8701	46.92919	< 0.0001
X ₃ ²	50.00263	1	50.00263	5.7674	0.0372
Residual	86.69873	10	8.669873		
Lack of Fit	68.113	5	13.6226	3.6648	0.0902
Pure Error	18.58573	5	3.717147		
Cor Total	3968.03	19			

In order to assess the correlations between parameters and to predict the result under given conditions, response surfaces and contour plots are generally used. The interaction effects of the variables used in this study on the response are graphically shown in Fig 4. Each three-dimensional surface plot represents the effects of two variables on the biodiesel conversion percent as a response, while the other variable is held constant at a zero level. The effects of catalyst dosage and methanol to oil molar ratio on conversion percent are shown in Figure 4A. The result indicated that the methanol to oil molar ratio exhibited more significant influence on the response surface compared to catalyst dosage. In heterogeneous catalysis, mass transfer and adsorption of reagents on the surface of catalyst are greatly important. Therefore, a methanol to oil molar ratio higher than that predicted from stoichiometry is necessary to shift the equilibrium to the products [24, 25]. An increase in the methanol to oil molar ratio resulted to an increase in the conversion (%), passing through a maximum around $M/O=24/1$ and decrease at higher molar ratio. Figure 4B represents the effect of reaction time and catalyst dosage on conversion percent. It was clear that higher catalyst amounts, as well as longer reaction times can increase the biodiesel production yield. However, conversion decreases at a high catalyst dosage, most probably due to the difficulty in mixing catalyst, reactant and product caused by the presence of excess catalyst [26]. Figure 4C illustrates the response of the interactive factor of methanol to oil molar ratio and reaction time. Based on the surface plots, the combined effect of the increased methanol to oil molar ratio and reaction time leads to the increment in biodiesel yield up to an optimum point. However, since transesterification is a reversible reaction high ratio of MeOH/oil would dilute the catalyst and reverse the reaction.

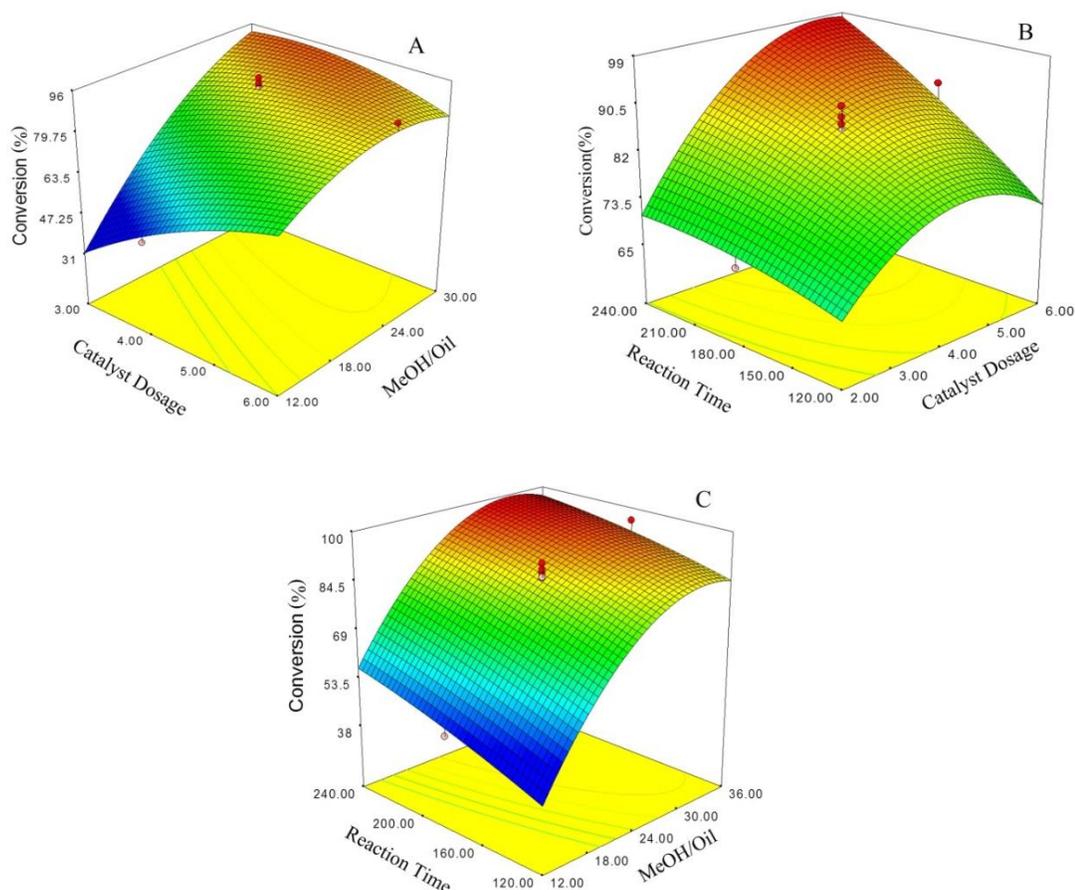


Figure 4. Response surface plot of combined effects of (A) catalyst dosage and methanol to oil molar ratios, (B) reaction time and catalyst dosage and (C) methanol to oil molar ratio and reaction time on the conversion percent of transesterification reaction. In each case other factor is held at zero level.

Optimization of biodiesel yield

The predicted optimum conditions for biodiesel production of sunflower oil by kanemite catalyst were suggested as follows: catalyst dosage 5 wt.%, methanol to oil molar ratio 22:1 and reaction time 240 min. Transesterification was carried out for three times at optimized conditions, and the average value on biodiesel was calculated. The predicted and experimental biodiesel conversions are reported as 95.97% and 94.17%, respectively, with 1.88% error. Thus, the optimized process conditions used in this study are verified.

Reusability of the catalyst

The reusability of prepared catalyst was investigated for transesterification of sunflower oil with methanol under optimum reaction conditions. After each run, the catalyst was separated by filtration and washed with n-hexane and methanol. Subsequently, catalyst was dried at 80 °C for 2h. After five consecutive recycles, the conversion decreased from 94.17% to 78.42% (Figure 5), suggesting that catalyst was efficient and reusable for production of biodiesel.

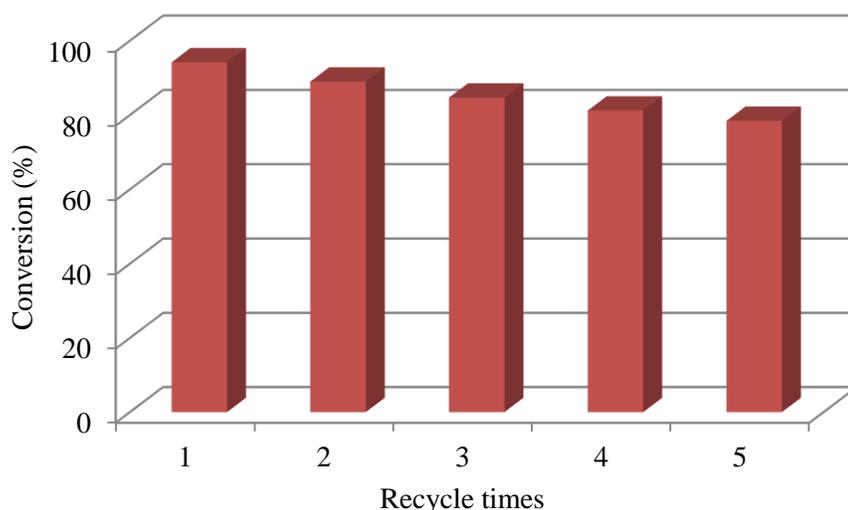


Figure 5. Effect of the recycling of catalyst on conversion of biodiesel (catalyst amount 5 wt.%, methanol/oil molar ratio 22:1 and reaction time 240 min).

Conclusion

In this study, kanemite was prepared using a simple procedure and used as a heterogeneous catalyst for biodiesel production from sunflower oil. Central Composite Design (CCD) coupled with Response Surface Methodology (RSM) was used to study the effects of the system variables such as catalyst amount, methanol to oil molar ratio and reaction time. Maximum conversion of biodiesel (94.17%) was obtained at methanol to oil ratio 22:1, catalyst amount of 5% and reaction time 240 min. After five reaction cycles, the catalyst still gave a high conversion of biodiesel (above 78%).

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References

- [1] S. H. Y. S. Abdullah, N. H. M. Hanapi, A. Azid, R. Umar, H. Juahir, H. Khatoun, A. Endut, *Renew. Sustain. Energy Rev.*, 70, 1040 (2017).
- [2] H. M. Mahmudul, F. Y. Hagos, R. Mamat, A. A. Adam, W. F. W. Ishak, R. Alenezi, *Renew. Sustain. Energy Rev.*, 72, 497 (2017).
- [3] F. Alzahar, *Int. J. New Chem.*, 4, 111 (2017).
- [4] M. R. Avhad, J. M. Marchetti, *Renew. Sustain. Energy Rev.*, 50, 696 (2015).
- [5] I. Atadashi, M. Aroua, A. Abdul Aziz, N. Sulaiman, *J. Ind. Eng. Chem.*, 19, 14 (2013).
- [6] W. Roschat, T. Siritanon, B. Yoosuk, V. Promarak, *Energy Convers. Manage.*, 119, 453 (2016).
- [7] A. K. Endalew, Y. Kiros, R. Zanzi, *Energy*, 36, 2693 (2011).
- [8] R. Shan, C. Zhao, H. Yuan, S. Wang, Y. Wang, *Energy Convers. Manage.*, 138, 547 (2017).
- [9] F. R. Panjaitan, S. Yamanaka, Y. Kuga, *Adv. Powder Technol.*, 28, 1627 (2017).
- [10] Y.C. Sharma, B. Singh, J. Korstad, *Fuel*, 90, 1309 (2011).
- [11] K. G. Georgogianni, A. P. Katsoulidis, P. J. Pomonis, M. G. Kontominas, *Fuel Process. Technol.*, 90, 671 (2009).
- [12] Y. Ren, B. He, F. Yan, H. Wang, Y. Cheng, L. Lin, Y. Feng, J. Li, *Bioresour. technol.*, 113, 19 (2012).
- [13] H. I. El Shimi, N. K. Attia, G. I. El Diwani, S. T. El Sheltawy, *Int. J. Energy Res.*, 40, 1743 (2016).
- [14] J. X. Wang, K. T. Chen, S. T. Huang, K. T. Chen, C. C. Chen, *J. Am. Oil Chem. Soc.*, 89, 1619 (2012).
- [15] F. Guo, Z. G. Peng, J. Y. Dai, Z. L. Xiu, *Fuel Process. Technol.*, 91, 322 (2010).
- [16] P. Guo, C. Zheng, M. Zheng, F. Huang, W. Li, Q. Huang, *Renew. Energy*, 53, 377 (2013).
- [17] L. A. J. Garvie, B. Devouard, T. L. Groy, F. Cámara, P. R. Buseck, *Am. Mineral.*, 84, 1170 (1999).
- [18] K. Beneke, G. Lagaly, *Am. Mineral.*, 62, 763 (1977).
- [19] M. D. Alba, P. Chain, E. Pavón, *Micropor. Mesopor. Mater.*, 94, 66 (2006).

- [20] W. W. S. Ho, H. K. Ng, S. Gan, S. H. Tan, *Energy Convers. Manage.*, 88, 1167 (2014).
- [21] S. Toriya, T. Takei, M. Fuji, M. Chikazawa, *J. Colloid Interface Sci.*, 268, 435 (2003).
- [22] Y. Huang, Z. Jiang, W. Schwieger, *Micropor. Mesopor. Mater.*, 26, 215 (1998).
- [23] Y. Huang, Z. Jiang, W. Schwieger, *Chem. Mater.*, 11, 1210 (1999).
- [24] J. Z. Yin, Z. Ma, D. P. Hu, Z. L. Xiu, T. H. Wang, *Energy Fuels*, 24, 3179 (2010).
- [25] K. T. Chen, J. X. Wang, Y. M. Dai, P. H. Wang, C. Y. Liou, C. W. Nien, J. S. Wu, C. C. Chen, *J. Taiwan Inst. Chem. Eng.*, 44, 622 (2013).
- [26] G. Y. Chen, R. Shan, J. F. Shi, B. B. Yan, *Fuel Process. Technol.*, 133, 8 (2015).

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