

NaOH impregnated sepiolite based heterogeneous catalyst and its utilization for the production of biodiesel from canola oil

Sema Aslan, Necdet Aka & M. Hamdi Karaoglu

To cite this article: Sema Aslan, Necdet Aka & M. Hamdi Karaoglu (2019) NaOH impregnated sepiolite based heterogeneous catalyst and its utilization for the production of biodiesel from canola oil, Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 41:3, 290-297, DOI: [10.1080/15567036.2018.1516010](https://doi.org/10.1080/15567036.2018.1516010)

To link to this article: <https://doi.org/10.1080/15567036.2018.1516010>



Published online: 05 Sep 2018.



Submit your article to this journal [↗](#)



Article views: 277



View related articles [↗](#)



View Crossmark data [↗](#)



Citing articles: 1 View citing articles [↗](#)



NaOH impregnated sepiolite based heterogeneous catalyst and its utilization for the production of biodiesel from canola oil

Sema Aslan, Necdet Aka, and M. Hamdi Karaoglu

Faculty of Science, Chemistry Department, Muğla Sıtkı Koçman University, Kötekli, Muğla, Turkey

ABSTRACT

NaOH/sepiolite nanocomposite heterogenous base catalyst (NaOH/sep.) was prepared via impregnation process and tested in a three-neck flask equipped with thermometer and reflux condenser for the production of biodiesel from transesterification of canola oil in an excess amount of methanol. The ratio of NaOH and sepiolite was selected as 1:4. The influence of various operational parameters was examined such as methanol to oil molar ratio, catalyst dosage, and reaction temperature. Untreated sepiolite and NaOH loaded sepiolite were characterized by X-ray diffraction, Fourier transform infrared spectroscopy, Scanning electron microscopy and Energy dispersive spectroscopy analysis. Overall NaOH/sep. based biodiesel production yield was examined by the help of Gas chromatography-mass spectrometry analysis. The yield was calculated from the peak areas as 80.93% which is better than that of expensive catalysis system using studies.

ARTICLE HISTORY

Received 11 April 2018
Revised 9 August 2018
Accepted 12 August 2018

KEYWORDS

Biodiesel production; Canola oil; heterogenous catalyst; nanocomposite renewable catalyst; sepiolite; transesterification

Introduction

As an environmentally friendly alternative energy, biodiesel has become a very intense research area received huge attention due to the restricted supply of conventional fossil fuel resources, increasing crude oil costs, and the exhaust gas emissions (Dang, Chen, and Lee 2013; Doyle et al. 2016; Kim et al. 2012; Liu et al. 2016; Patel, Brahmkhatri, and Singh 2013). Biodiesel commonly consists of the methyl esters of a mixture of long-chain fatty acids that can be produced from divergent types of oils, mostly plant oils, such as coconut, palm or soybean oils. Also, they can be produced from recycled cooking oil or animal fats (Kusuma et al. 2013; Uriatre 2010). Biodiesel can be produced in the presence of various kinds of catalysts, such as homogeneous catalysts (alkali metal hydroxide, different acid, etc.) and heterogeneous catalysts (modified clay, cation-exchange resin, hydrotalcites, etc.), and enzymes (Dehkordi and Ghasemi 2012; Margaretha et al. 2012). Heterogeneous catalysts have been preferred for the biodiesel production studies due to their regeneration capability and ease of separation from reaction products (Olutoye and Hameed 2013). Modified catalyst provides a way to be used as a suspension in the liquid solution medium. In this manner different types of heterogenous catalysts have been used to produce biodiesel such as calcium supported tin oxide (Xie and Zhao 2013), graphene oxide-Fe₃O₄ nanocomposite support (Xie and Huang 2018), Fe₃O₄/Poly(styrene-methacrylic acid) based magnetic microsphere (Xie and Wang 2014), aminopropyl-functionalized hydroxyapatite-encapsulated- α -Fe₂O₃ nanoparticles as magnetic biocatalyst (Xie and Zang 2017), biguanide-functionalized hydroxyapatiteencapsulated- γ -Fe₂O₃ nanoparticles (Xie, Han, and Tai 2017) and ionic liquid functionalized magnetic composites (Xie and Wan 2018). Among these available heterogenous catalysts, modified sepiolite finds wider application area because of its relatively high active surface area, biological and chemical inertness and stability, cost-effectiveness and non-toxic nature (Muthirulan, Meenakshisundaram, and Kannan 2013).

CONTACT M. Hamdi Karaoglu  khamdi@mu.edu.tr  Faculty of Science, Chemistry Department, Muğla Sıtkı Koçman University, Kötekli, Muğla 48000, Turkey

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/ueso.

In this study, NaOH/sep. catalyst was introduced as a novel and effective catalyst for the production of biodiesel from transesterification of canola oil. Some of the catalytic parameters of the reactions that effects the yield of the process such as catalyst dosage, methanol to oil molar ratio and temperature of the reaction were investigated. In addition, the modified catalyst was characterized by Scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) analysis.

Experimental

Catalyst preparation and characterization

The modified catalyst was synthesized via wet impregnation of an aqueous solution of potassium hydroxide salt and sepiolite as a support. The ratio between NaOH and sepiolite was selected as 1:4. The synthesis of the catalyst was carried out in a three-neck round bottom flask (500 mL) equipped with a thermometer, reflux condenser, and mechanical stirrer. The impregnation step of sepiolite with NaOH was performed at a temperature of 60°C for 24 h under continuous stirring conditions. After the impregnation process was finished, the material was filtrated and dried and then calcined under static air at 500°C for 5 h. Then, these samples were transferred into a desiccator, cooled, and kept in dark medium when not in use (Omar and Amin 2011; Soetaredjo et al. 2011). The morphological and structural properties of the catalyst were investigated by FT-IR, XRD, SEM, and EDS analysis.

Transesterification reaction and analysis methods of biodiesel

The mixture of methanol, canola oil and a small quantity of modified catalyst were transferred into a reflux condenser adapted three-neck flask at 60°C temperature and a chronometer was run spontaneously. The contents were stirred in these conditions for 3 h then the mixture was cooled down to the room temperature. Subsequently, obtained samples were centrifuged for 15 min at 5000 rpm and the left out concentration in the supernatant solution was washed and dried with natrium sulfate anhydrous and then analyzed by GC-MS (Omar and Amin 2011). According to the spectrum obtained from GC-MS analysis, obtained fatty acid methyl esters and the percentages were determined and given in Table 1. The peak areas of these methyl esters were used for the biodiesel yield calculation as given as Eq. (1) (Wan et al. 2009).

$$\text{Biodiesel yield} = (m_1 \times A_1) / (m_2 \times A_2) \times 100\% \quad (1)$$

m_1 ; the weight of the internal standard, m_2 ; the weight of the biodiesel, A_1 ; the area of the total internal standard and A_2 ; the area of the total fatty acid methyl esters obtained from soybean oil. All of the biodiesel experiments were performed twice.

Table 1. Properties of the final biodiesel eluted from the reactor after transesterification process.

Fatty acid methyl ester type	Unit quantity of the product (w%)
Methyl oleate	59.949
Methyl linoleate	20.019
Methyl palmitate	4.720
Methyl linolenate	4.497
Methyl elaidate	3.286
Methyl heneicosanoate	1.667
Methyl stearate	0.149
Methyl cis-11-eicosenoate	0.870
Methyl butyl-9-tetradecenoate	2.667
Total Fatty acid methyl ester amount	95.13

Materials

Chemicals

Methanol (99.8% pure), n-hexane (99.0% pure), sodium sulfate (99% pure) and sodium hydroxide (99% pure) were purchased from Merck Co. Sepiolite was supplied by Sigma Co. Edible grade canola oil was obtained from a local market (Kipa Co.).

Results and discussion

FT-IR spectroscopy analysis

The FT-IR spectra of raw sepiolite and NaOH/sep. were presented in Figure 1a,b, respectively. The FT-IR spectrums of the raw sepiolite and NaOH/sep. show the presence of functional groups such as the OH vibration of the external surface (3451.62 and 3428.77 cm^{-1}), the OH-bending of zeolitic water (1644.83 and 1653.21 cm^{-1}), the hydroxyl bending vibration (1426.17 and 1434.06 cm^{-1}), the Si—O—Si plane vibrations (1000 cm^{-1}) (Cobas et al. 2014; Eren et al. 2010).

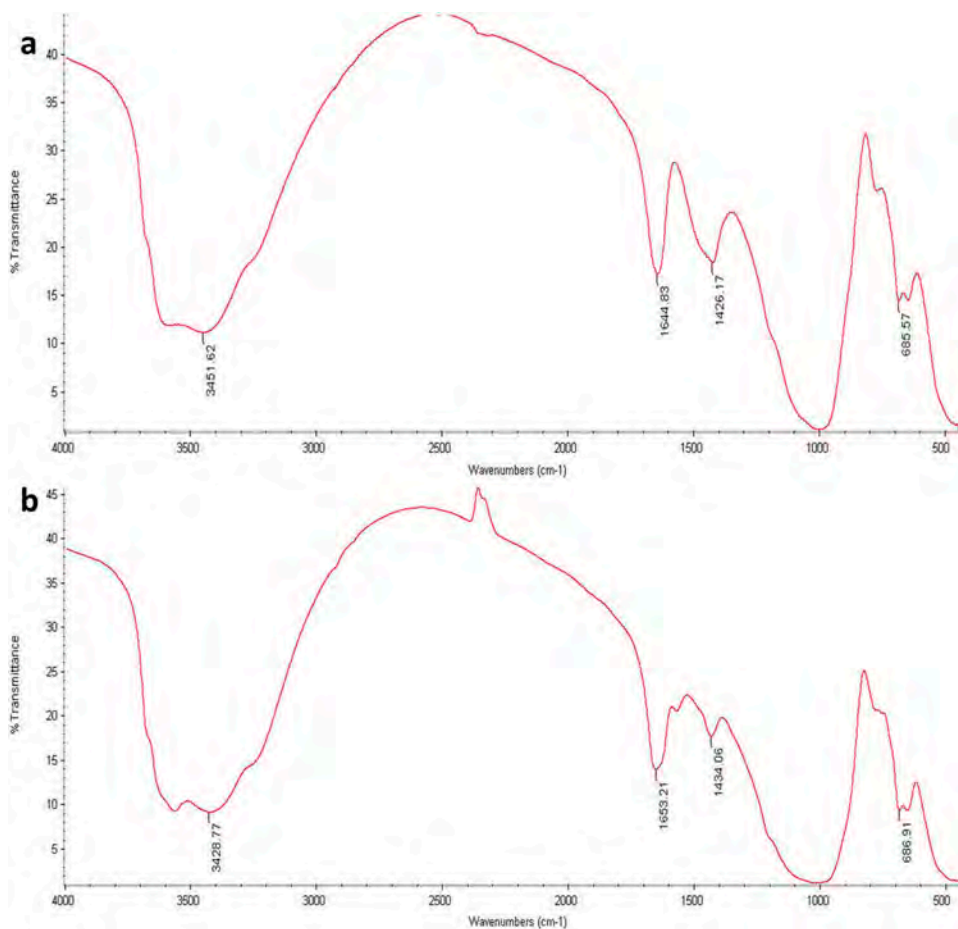


Figure 1. FT-IR spectra of a) raw sepiolite and b) NaOH/sep. catalyst after the impregnation.

SEM and EDS analysis

Figure 2 shows SEM and EDS images of the raw and modified sepiolites. The impregnation of sepiolite with NaOH is determined quantitatively by using the EDS elemental analysis of raw sepiolite and NaOH/sep. catalyst. The atomic weight percentages of the elements that are present in the composition of raw sepiolite, determined as 13.19% for magnesium, 57.98% for oxygen, 24.62% for silicon and 0.68% for aluminum. However, after impregnation of with NaOH and calcination, the elemental composition shows magnesium 14.36%, oxygen 51.46%, silicon 26.97%, aluminum 0.38%, and natrium 3.33%. According to these results, the change in the elemental composition of raw sepiolite is attributed to the successful impregnation with NaOH on the surface of sepiolite and proves that the synthesized structure is a nanocomposite heterogenous NaOH/sep. catalyst.

XRD analysis of raw sepiolite and NaOH/sep

XRD curves of raw sepiolite (Figure 3a) and NaOH/sep. (Figure 3b) are discussed. The diffraction signals of natural sepiolite coincide well with the structure ($2\theta = 7.14; 13.09; 20.51; 26.57; 33.21; 34.99; 36.63; 43.88; 58.08$ and 61.71°). Peaks at 8.55 and 10.95° were also observed, which indicates the sepiolite anhydride formation through the calcination process at the temperature of 500°C . Other diffraction peaks define different oxides which have already been in the natural sepiolite structure (Milt et al. 2010).

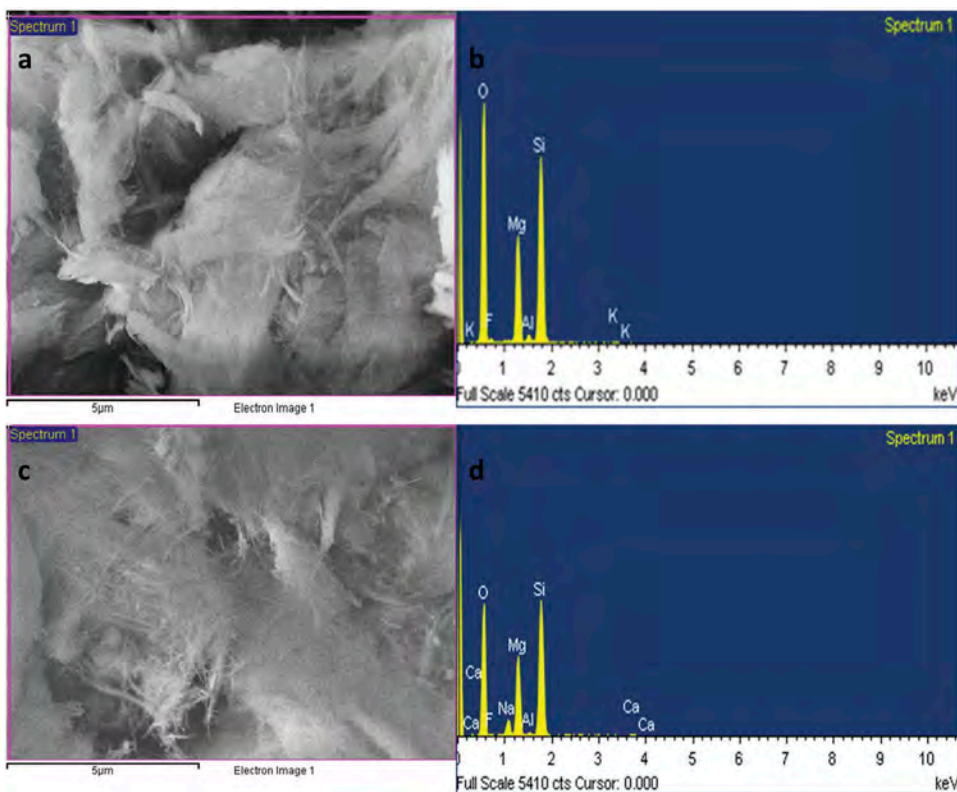


Figure 2. a) SEM, b) EDS images of raw sepiolite, c) SEM, d) EDS images of NaOH/sep. catalyst.

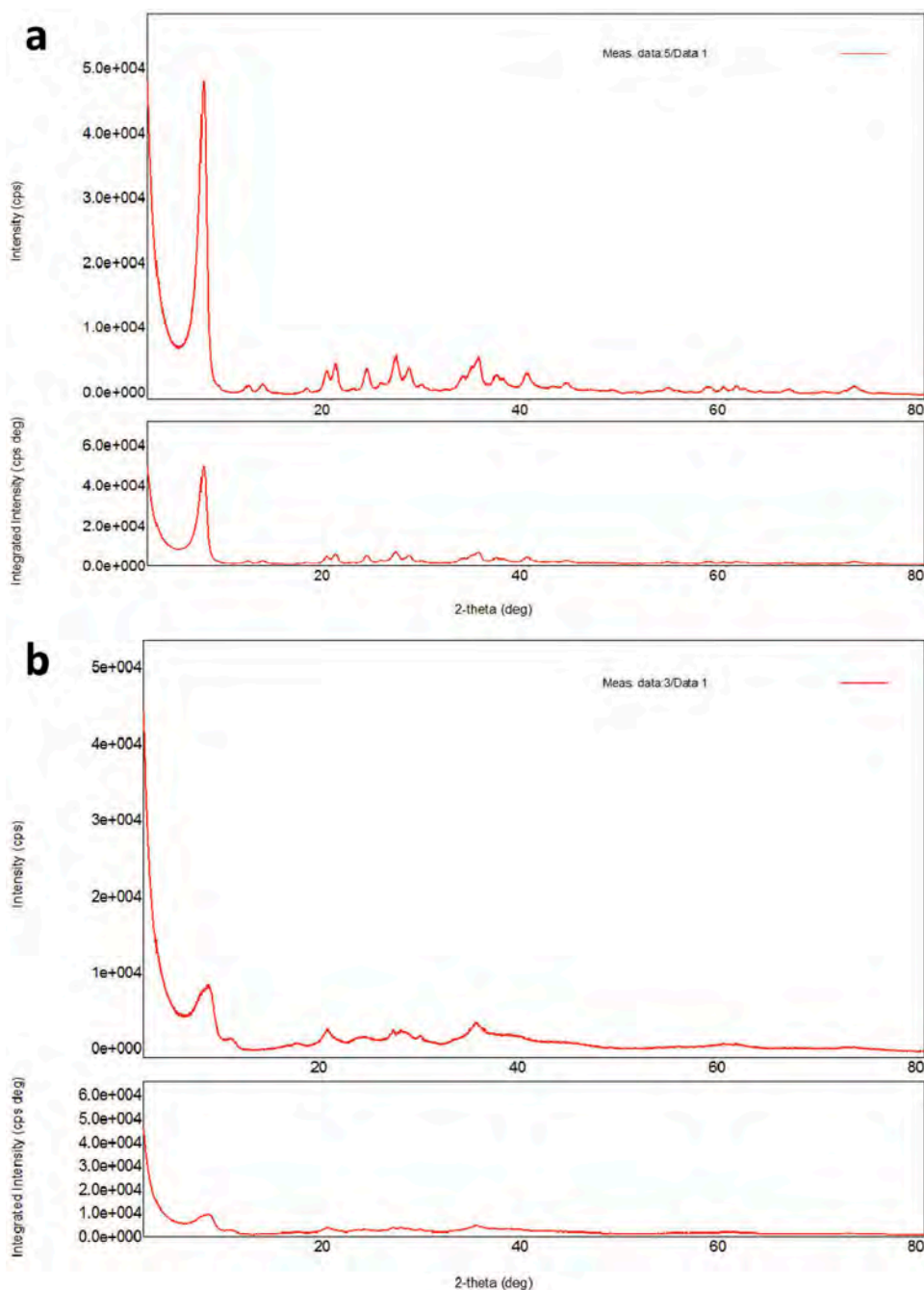
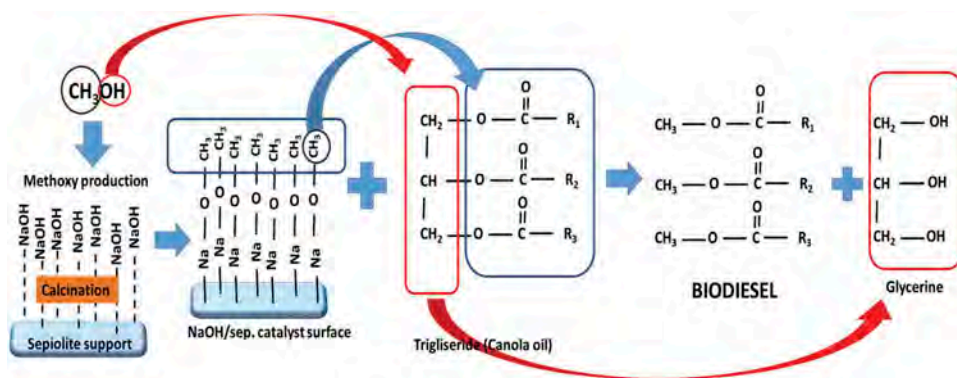


Figure 3. XRD patterns of a) raw sepiolite and b) NaOH/sep. catalyst.

Evaluation of the catalytic performance of NaOH/sep. modified catalyst

Schematic illustration of the NaOH/sep. catalyst synthesis and the transesterification process is presented in [Scheme 1](#). After the synthesis and the characterization studies, catalytic parameters of heterogeneous catalyst was enlightened.



Scheme 1. Schematic representation of the impregnation of NaOH onto sepiolite and mechanism of transesterification process on NaOH/sep. heterogenous catalyst.

GC-MS analysis results of the biodiesel that was synthesized at the optimum conditions are shown in Table 1. According to the related methyl ester total yield, it is very satisfying to reach 95.13% points in such a simple synthesis system.

The effect of catalyst dosage on the biodiesel yield

The amount of the catalyst is a key point of biodiesel production. Since the reaction yields improved by expanding the catalyst surface area the effect of the catalyst amount on the biodiesel yield was studied by varying catalyst weights from 1.5% to 6% (Figure 4a). In the end of the experiments, the biodiesel yield clearly increased from 67.23% to 80.93% in accordance with the increment of the catalyst amount. It seems that 1.5% is the optimal catalyst amount and the number of active sites is much more at than that of at 6% one (Shahraki, Entezari, and Goharshadi 2015).

The effect of transesterification temperature on the biodiesel yield

The temperature has an important effect on base-catalyzed transesterification reaction (Takase et al. 2014). In order to prevent the occurrence of undesired by-products such as unsaturated fatty acid methyl esters or saponification, it is crucial to find out the optimum reaction temperature of esterification. Here, the effect of temperature on the reaction has been investigated for different values as 50°C, 60°C, and 70°C. The methanol/oil molar ratio of 9:1 and catalyst concentration of 3% (w/w) were utilized for all the experiments. Figure 4b shows the conversion rate of biodiesel increased by the reaction temperature increased up to 60°C then deactivation was observed due to the further temperature increment. It has been used as an optimum temperature value for several previous studies (Abba et al. 2017; Takase et al. 2014) and the deactivation was claimed in detail. So 60°C was determined as the optimum temperature for the following experiments.

The effect of methanol/oil molar ratio on the biodiesel yield

Since the biodiesel production from transesterification is a reversible reaction, the total yield of biodiesel could be improved. For this purpose, the excess amounts of methanol can be introduced to the medium to force the biodiesel formation reaction (Wu et al. 2013). In order to explain the effect of the methanol/oil molar ratio phenomenon on the biodiesel production yield, different amounts of methanols were selected varying from 3:1 to 12:1. During these experiments the catalyst amount was 3 wt.%, reaction time maintained 180 min and the temperature was 60°C. After the experiments, the yield increased from 60.56% to 73.69% with the increase in a molar ratio from 3:1 to 9:1 (Figure 4c).

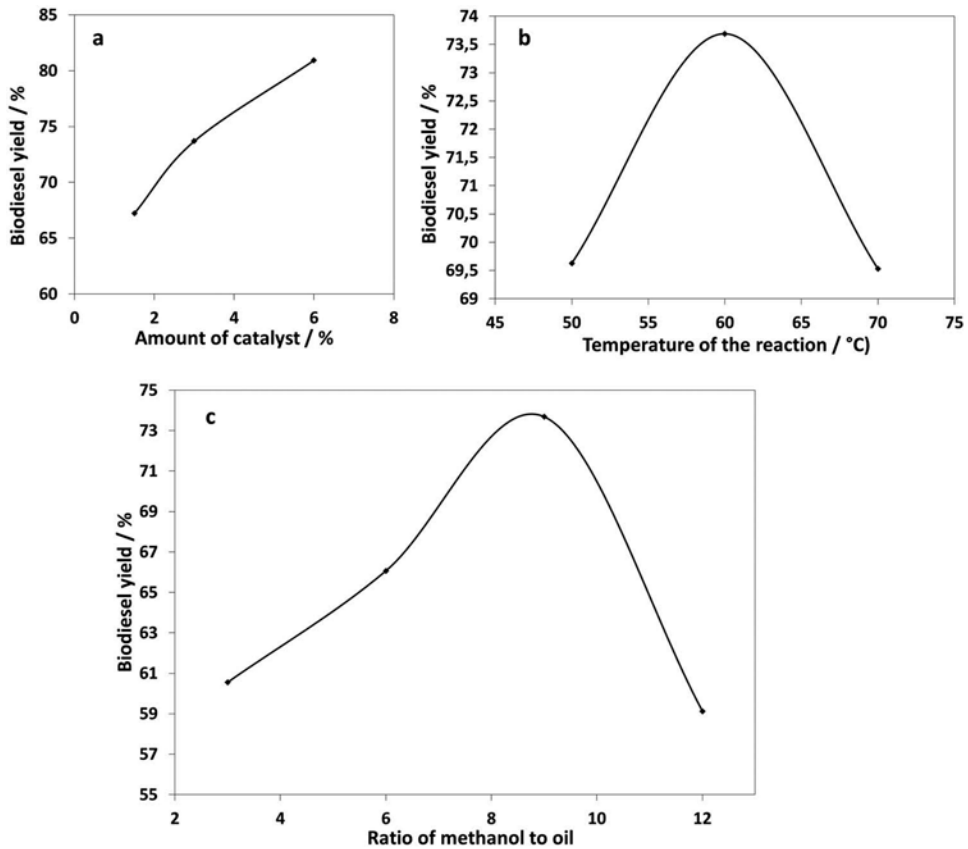


Figure 4. Catalytic performance studies and evaluation of the effect of a) catalyst amount, b) reaction temperature, c) methanol to oil ratio on the biodiesel production performance of NaOH/sep. catalyst.

Conclusions

Overall, biodiesel is successfully produced from canola oil using NaOH/sep. catalyst using transesterification process. Optimum conditions were obtained for a 180 min transesterification reaction for methanol/oil molar ratio of 9:1, amount of catalyst of 6.0 wt.% and reaction temperature at 60°C, achieving biodiesel yield of 80.93%. This yield output could be improved by the implementation of the further pretreatment processes and also regeneration performance of the produced catalyst should be examined. Presented conditions are planned to be improved by the usage of different improved transesterification methods such as microwave assisted systems, different than reflux adapted ones.

Acknowledgment

The authors are grateful to the Mugla Sıtkı Kocman University Research Fund (13/125) for financing this research.

References

- Abba, E. C., N. R. Nwakuba, S. N. Obasi, and J. I. Enem. 2017. Effect of reaction time on the yield of biodiesel from Neem Seed Oil. *American Journal of Energy Science* 4:5–9.
- Cobas, M., L. Ferreira, M. A. Sanroman, and M. Pazos. 2014. Assessment of sepiolite as a low-cost adsorbent for phenanthrene and pyrene removal: Kinetic and equilibrium studies. *Ecological Engineering* 40:287–94. doi:10.1016/j.ecoeng.2014.06.014.

- Dang, T. H., B.-H. Chen, and D.-J. Lee. 2013. Application of kaolin-based catalysts in biodiesel production via transesterification of vegetable oils in excess methanol. *Bioresource Technology* 145:175–81. doi:10.1016/j.biortech.2012.12.024.
- Dehkordi, A. M., and M. Ghasemi. 2012. Transesterification of waste cooking oil to biodiesel using Ca and Zr mixed oxides as heterogeneous base catalysts. *Fuel Proceeding Technology* 97:45–51. doi:10.1016/j.fuproc.2012.01.010.
- Doyle, A. M., T. M. Albayati, A. S. Abbas, and Z. T. Alismael. 2016. Biodiesel production by esterification of oleic acid over zeolite Y prepared from kaolin. *Renewable Energy* 97:19–23. doi:10.1016/j.renene.2016.05.067.
- Eren, E., O. Cubuk, H. Ciftci, B. Eren, and B. Caglar. 2010. Adsorption of basic dye from aqueous solutions by modified sepiolite: Equilibrium, kinetics and thermodynamics study. *Desalination* 252:88–96. doi:10.1016/j.desal.2009.10.020.
- Uriarte, Filomen A., Jr. 2010. *Biofuels from plant oils*. Indonesia: ASEAN Foundation.
- Kim, M., C. DiMaggio, S. O. Salley, and K. Y. S. Ng. 2012. A new generation of zirconia supported metal oxide catalysts for converting low grade renewable feedstocks to biodiesel. *Bioresource Technology* 118:37–42. doi:10.1016/j.biortech.2012.04.035.
- Kusuma, R. I., J. P. Hadinoto, A. Ayucitra, F. E. Soetaredjo, and S. Ismadji. 2013. Natural zeolite from Pacitan Indonesia, as catalyst support for transesterification of palm oil. *Applied Clay Science* 74:121–26. doi:10.1016/j.clay.2012.04.021.
- Liu, H., H. S. Guo, X. J. Wang, J. Z. Jiang, H. Lin, S. Han, and S. P. Pei. 2016. Mixed and ground KBr-impregnated calcined snail shell and kaolin as solid base catalysts for biodiesel production. *Renewable Energy* 93:648–57. doi:10.1016/j.renene.2016.03.017.
- Margaretha, Y. Y., H. S. Prastyo, A. Ayucitra, and S. Ismadji. 2012. Calcium oxide from Pomacea sp. shell as a catalyst for biodiesel production. *International Journal of Energy and Environmental Engineering* 3 (33):1–9. doi:10.1186/2251-6832-3-33.
- Milt, V. G., E. D. Banús, E. E. Miró, M. Yates, J. C. Martín, S. B. Rasmussen, and P. Ávila. 2010. Structured catalysts containing Co, Ba and K supported on modified natural sepiolite for the abatement of diesel exhaust pollutants. *Chemical Engineering Journal* 157:530–38. doi:10.1016/j.cej.2009.12.049.
- Muthirulan, P., M. Meenakshisundaram, and N. Kannan. 2013. Beneficial role of ZnO photocatalyst supported with porous activated carbon for the mineralization of alizarin cyanin green dye in aqueous solution. *Journal of Advanced Research* 4:479–84. doi:10.1016/j.jare.2012.08.005.
- Olutoye, M. A., and B. H. Hameed. 2013. Production of biodiesel fuel by transesterification of different vegetable oils with methanol using Al₂O₃ modified MgZnO catalyst. *Bioresource Technology* 132:103–08. doi:10.1016/j.biortech.2012.12.171.
- Omar, W. N. N. W., and N. A. S. Amin. 2011. Biodiesel production from waste cooking oil over alkaline modified zirconia catalyst. *Fuel Proceeding Technology* 92:2397–405. doi:10.1016/j.fuproc.2011.08.009.
- Patel, A., V. Brahmkhatri, and N. Singh. 2013. Biodiesel production by esterification of free fatty acid over sulfated zirconia. *Renewable Energy* 51:227–33. doi:10.1016/j.renene.2012.09.040.
- Shahraki, H., M. H. Entezari, and E. K. Goharshadi. 2015. Sono-synthesis of biodiesel from soybean oil by KF/c-Al₂O₃ as a nano-solid-base catalyst. *Ultrasonics Sonochemistry* 23:266–74. doi:10.1016/j.ultsonch.2014.10.001.
- Soetaredjo, F. E., A. Ayucitra, S. Ismadji, and A. L. Maukar. 2011. KOH/bentonite catalysts for transesterification of palm oil to biodiesel. *Applied Clay Science* 53:341–46. doi:10.1016/j.clay.2010.12.018.
- Takase, M., Y. Chen, H. Liu, T. Zhao, L. Yang, and X. Wu. 2014. Biodiesel production from non-edible Silybum marianum oil using heterogeneous solid base catalyst under ultrasonication. *Ultrasonics Sonochemistry* 21:1752–62. doi:10.1016/j.ultsonch.2013.10.002.
- Wan, T., P. Yu, S. Wang, and Y. Luo. 2009. Application of sodium aluminate as a heterogeneous base catalyst for biodiesel production from soybean oil. *Energy Fuels* 23 (2):1089–92. doi:10.1021/ef800904b.
- Wu, H., J. Zhang, Q. Wei, J. Zheng, and J. Zhang. 2013. Transesterification of soybean oil to biodiesel using zeolite supported CaO as strong base catalysts. *Fuel Proceeding Technology* 109:13–18. doi:10.1016/j.fuproc.2012.09.032.
- Xie, W., Y. Han, and S. Tai. 2017. Biodiesel production using biguanide-functionalized hydroxyapatite-encapsulated-γ-Fe₂O₃ nanoparticles. *Fuel* 210:83–90. doi:10.1016/j.fuel.2017.08.054.
- Xie, W., and M. Huang. 2018. Immobilization of Candida rugosa lipase onto graphene oxide Fe₃O₄ nanocomposite: Characterization and application for biodiesel production. *Energy Conversion and Management* 159:42–53. doi:10.1016/j.enconman.2018.01.021.
- Xie, W., and F. Wan. 2018. Basic ionic liquid functionalized magnetically responsive Fe₃O₄@HKUST-1 composites used for biodiesel production. *Fuel* 220:248–56. doi:10.1016/j.fuel.2018.02.014.
- Xie, W., and J. Wang. 2014. Enzymatic production of biodiesel from soybean oil by using immobilized lipase on Fe₃O₄/Poly(styrene-methacrylic acid) magnetic microsphere as a biocatalyst. *Energy Fuels* 28:2624–2631. doi:10.1021/ef500131s.
- Xie, W., and X. Zang. 2017. Covalent immobilization of lipase onto aminopropyl-functionalized hydroxyapatite-encapsulated-γ-Fe₂O₃ nanoparticles: A magnetic biocatalyst for interesterification of soybean oil. *Food Chemistry* 227:397–403. doi:10.1016/j.foodchem.2017.01.096.
- Xie, W., and L. Zhao. 2013. Production of biodiesel by transesterification of soybean oil using calcium supported tin oxides as heterogeneous catalysts. *Energy Conversion and Management* 76:55–62. doi:10.1016/j.enconman.2013.07.027.