

Efficiency of Sulfonated UiO-66 on Biodiesel Production from Oleic Acid: An Optimization Study with ANCOVA [†]

Gamze Ozcakil

Department of Chemical Engineering, Faculty of Engineering, Bilecik Seyh Edebali University, TR 11100 Bilecik, Turkey; gamze.ozcakil@bilecik.edu.tr

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Abstract: Biodiesel is defined as a mixture of fatty acids and methyl esters. Using waste cooking oils as raw material can prefer an acidic catalyst to carry out an esterification reaction in biodiesel production. Researchers have generally used heterogeneous sulfonated solid catalysts for this reaction. However, the by-product water, the result of the biodiesel production process, absorbs on the catalyst surface. So, it is crucial to select hydrophobic support. To use sulfonated UiO-66 for biodiesel production via the esterification of waste cooking oil is logical. Besides its hydrophobicity, it knows that UiO-66 has high chemical and thermal stability, high surface area, and uniform pore structure. The study aims to determine the effective parameter in biodiesel synthesis from oleic acid esterification on sulfonated UiO-66 with ANCOVA analysis. For optimization analysis, Sigma Plot 14.0 software was utilized as software. Holm-Sidak test was applied for one-way ANCOVA. Parameters were effective on the oleic acid conversion rate selected as esterification temperature, time, catalyst amount, and methanol/oleic acid rate.

Keywords: oleic acid; esterification; biodiesel; metal-organic framework

1. Introduction

Biodiesel has renewable, biodegradable, non-toxic features, and forms a suitable alternative to fossil fuels. Besides that, biodiesel can be used in automobiles. In addition, by using biodiesel in transportation widely, it can be possible to reduce environmental waste and fuel prices [1].

Biodiesel composes of methyl esters. These methyl esters form result of a transesterification reaction between oils and methanol. As an oil source, edible and non-edible materials, and waste cooking oils can be used for biodiesel production. Using waste cooking oils as a feedstock is preferred. In this way, waste management made. Besides, the feedstock is global not a local product like rapeseed or palm oil which means that transportation does not need [2].

Homogenous or heterogeneous catalysts can be used for biodiesel production from waste cooking oils via transesterification reaction improving reaction rate and yield. Homogenous catalysts can be base or acid. Basic ones can be sodium (NaOH) or potassium hydroxide (KOH). Acidic ones can be sulphuric (H₂SO₄), hydrochloric acid (HCl), etc. Basic homogenous catalysts have high efficiency. However, soap formation can occur on the catalysts. Heterogeneous catalysts can be recovered readily from the medium after the reaction. They are cheaper than homogenous ones. In addition, soap formation does not occur on heterogeneous catalysts. Samely, basic catalysts show higher catalytic efficiency than acidic catalysts in heterogeneous catalysts. However, they can require working higher reaction temperatures and longer times. Examples of heterogeneous acidic catalysts are sulfated metal oxide, heteropolyacids, acidic ion exchange resin, and sulfonated amorphous catalysts [3].

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In industry, the high oleic acid content of vegetable oil such as sunflower, soybean, and rapeseed is important [4]. There are many types of research in the literature to be used sulfonated heterogeneous catalysts like zeolites, bio-chars, and metal-organic frameworks (MOFs) for biodiesel production from oleic acid [5–10]. MOFs are crucial porous materials whose surface area and pore size can be up to nearly 10,000 m²/g and 10 nm. UiO-66 is one of the types of MOFs. It contains Zirconium (Zr) as a metal ion and terephthalate as an organic ligand. Its crystalline structure is stable up to 500 °C. Besides, UiO-66 has resistance to high alkaline and acidic conditions. This is a novel approach in literature to utilize sulfonated UiO-66 in biodiesel synthesis from oleic acid [11–14]. This study aimed to determine the most effective parameters on biodiesel production from oleic acid by using sulfonated UiO-66 via ANCOVA computational analysis.

2. Materials and Method

The software utilized for the optimization study was SigmaPlot 14.0. One way ANCOVA was selected to carry out the analysis. The Holm-Sidak test was used for the calculations. For normality, the Kolmogorov-Smirnov test was utilized. The Levene test was used to compute the equal variance. Result of the analysis, the independent variables were catalyst amount, temperature, time, and methanol/oleic acid ratio connected dependent variable (oleic acid conversion rate) with equations. The importance of the independent variables on the oleic acid conversion rate evaluated concerning *p* values means that a variable possessed below 0.015 *p*-value, the effect of this variable on the oleic acid conversion rate was crucial. Taken data for the computational study were given in Table 1.

Table 1. Data for producing biodiesel from oleic acid via sulfonated UiO-66.

Temperature (°C)	Time (h)	Catalyst Amount (wt.%)	Methanol/Oleic Acid Molar Ratio	Reference
50–60–70–80–90	0.5–1–1.5–2–3–4–5	4–6–8–10–12	6–8–10–12–14	Li et al. (2021a) [15]
70–80–90–100–110	0.5–0.7–0.8–1.0–1.2	2–4–6–8–10	5–10–15–20–25	Gouda et al. (2022) [12]
60–65–70–75–80	0.5–1–1.5–2–2.5	4–6–8–10–12	4–6–8–10–12	Li et al. (2021b) [16]

3. Results and Discussion

ANCOVA analysis applied to sulfonated UiO-66 catalyst for biodiesel production from oleic acid. Table 2 shows ANCOVA results for this catalyst. Catalyst amount was determined as a factor and, other parameters were time, methanol/oleic acid ratio and, temperature accepted as covariates. As shown in the results, parameters except for temperature had a crucial effect on biodiesel production. ANCOVA analysis of sulfonated UiO-66, the R² was found as 0.402. Figure 1 shows the possible oleic acid conversion ranges when it utilized a suitable amount of catalyst.

Table 3 presents the equations for biodiesel generation on sulfonated UiO-66. So, it can easily predict biodiesel generation for oleic acid conversion rate without extra catalytic tests.

Table 2. ANCOVA results for producing biodiesel from oleic acid via sulfonated UiO-66.

Variance Source	Degree of Freedom	Sum of Square	Mean Square Value	F-Value	<i>p</i> -Value
<i>Catalyst amount (wt.%)</i>	5	1138.589	227.718	3.126	0.015
<i>Temperature (°C)</i>	1	174.536	174.536	2.396	0.128
<i>Time (h)</i>	1	807.785	807.785	11.088	0.002

<i>Methanol/Oleic Acid Molar Ratio</i>	1	909.085	909.085	12.479	<0.001
<i>Residual</i>	53	3861.085	72.851	--	--
<i>Total</i>	61	6457.242	105.856	--	--

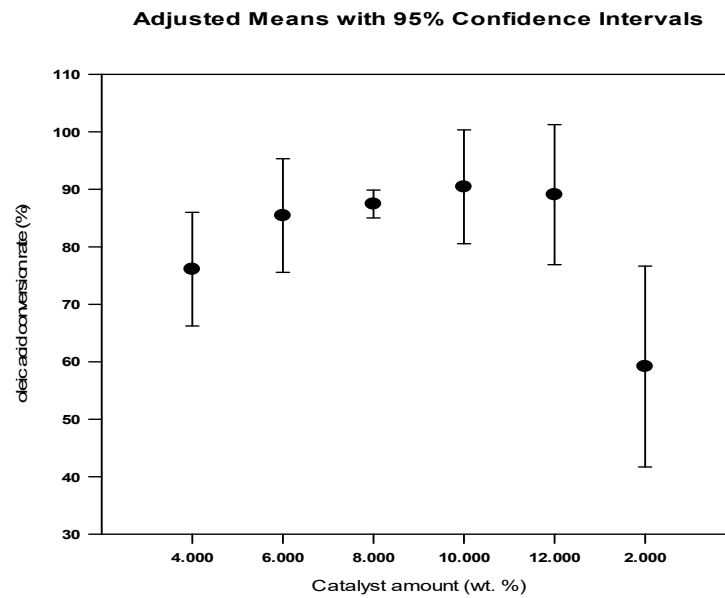


Figure 1. Adjusted means with 95% confidence intervals for sulfonated UiO-66.

Table 3. Resulting ANCOVA equations for producing biodiesel from oleic acid via sulfonated UiO-66.

<i>Catalyst Amount (wt.%)</i>	<i>Equations</i>
2	oleic acid conversion rate (%) = 50.061 – (0.185 × Temperature (°C)) + (5.836 × Time (h)) + (1.132 × Methanol/Oleic acid molar ratio)
4	oleic acid conversion rate (%) = 67.010 – (0.185 × Temperature (°C)) + (5.836 × Time (h)) + (1.132 × Methanol/Oleic acid molar ratio)
6	oleic acid conversion rate (%) = 76.343 – (0.185 × Temperature (°C)) + (5.836 × Time (h)) + (1.132 × Methanol/Oleic acid molar ratio)
8	oleic acid conversion rate (%) = 78.364 – (0.185 × Temperature (°C)) + (5.836 × Time (h)) + (1.132 × Methanol/Oleic acid molar ratio)
10	oleic acid conversion rate (%) = 81.343 – (0.185 × Temperature (°C)) + (5.836 × Time (h)) + (1.132 × Methanol/Oleic acid molar ratio)
12	oleic acid conversion rate (%) = 79.985 – (0.185 × Temperature (°C)) + (5.836 × Time (h)) + (1.132 × Methanol/Oleic acid molar ratio)

4. Conclusions

This work aimed to see the effect of parameters on oleic acid conversion for biodiesel production on sulfonated UiO-66 catalysts. Experimental data obtained from the literature. Then, data was utilized in the analysis of covariance (ANCOVA). After then, they revealed the effective parameters in the experiments on the oleic acid conversion rate to biodiesel, which range can be used for the production of sulfonated UiO-66 catalyst, and the equations which enabled the relationship between dependent and independent variables.

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References

1. Xie, W.; Li, J. Magnetic solid catalysts for sustainable and cleaner biodiesel production: A comprehensive review. *Renew. Sustain. Energy Rev.* **2023**, *171*, 113017.
2. Taddeo, F.; Vitiello, R.; Russo, V.; Tesser, R.; Turco, R.; Di Serio, M. Biodiesel Production from Waste Oil Catalysed by Metal-Organic Framework (MOF-5): Insights on Activity and Mechanism. *Catalysts* **2023**, *13*, 503.
3. Yaakob, Z.; Mohammad, M.; Alherbawi, M.; Alam, Z.; Sopian, K. Overview of the production of biodiesel from waste cooking oil. *Renew. Sustain. Energy Rev.* **2013**, *18*, 184–193.
4. Matthäus, B. Utilization of high-oleic rapeseed oil for deep-fat frying of French fries compared to other commonly used edible oils. *Eur. J. Lipid Sci. Technol.* **2006**, *108*, 200–211.
5. Niu, S.; Ning, Y.; Lu, C.; Han, K.; Yu, H.; Zhou, Y. Esterification of oleic acid to produce biodiesel catalyzed by sulfonated activated carbon from bamboo. *Energy Convers. Manag.* **2018**, *163*, 59–65.
6. Wang, Y.T.; Yang, X.X.; Xu, J.; Wang, H.L.; Wang, Z.B.; Zhang, L.; Liang, J.L. Biodiesel production from esterification of oleic acid by a sulfonated magnetic solid acid catalyst. *Renew. Energy* **2019**, *139*, 688–695.
7. Marzouk, N.M.; El Naga, A.O.A.; Younis, S.A.; Shaban, S.A.; El Torgoman, A.M.; El Kady, F.Y. Process optimization of biodiesel production via esterification of oleic acid using sulfonated hierarchical mesoporous ZSM-5 as an efficient heterogeneous catalyst. *J. Environ. Chem. Eng.* **2021**, *9*, 105035.
8. Gecgel, C.; Turabik, M. Synthesis and sulfonation of an aluminum-based metal–organic framework with microwave method and using for the esterification of oleic acid. *J. Inorg. Organomet. Polym. Mater.* **2021**, *31*, 4033–4049.
9. Yılmaz, E.; Sert, E.; Atalay, F.S. Synthesis and sulfation of titanium based metal organic framework; MIL-125 and usage as catalyst in esterification reactions. *Catal. Commun.* **2017**, *100*, 48–51.
10. Pang, H.; Yang, G.; Li, L.; Yu, J. Esterification of oleic acid to produce biodiesel over 12-tungstophosphoric acid anchored two-dimensional zeolite. *Chem. Res. Chin. Univ.* **2021**, *37*, 1072–1078.
11. Liu, W.; Wang, F.; Meng, P.; Zang, S.Q. Sulfonic Acids Supported on UiO-66 as Heterogeneous Catalysts for the Esterification of Fatty Acids for Biodiesel Production. *Catalysts* **2020**, *10*, 1271.
12. Gouda, S.P.; Ngaosuwan, K.; Assabumrungrat, S.; Selvaraj, M.; Halder, G.; Rokhum, S.L. Microwave assisted biodiesel production using sulfonic acid-functionalized metal-organic frameworks UiO-66 as a heterogeneous catalyst. *Renew. Energy* **2022**, *197*, 161–169.
13. Lu, P.; Li, H.; Li, M.; Chen, J.; Ye, C.; Wang, H.; Qiu, T. Ionic liquid grafted NH₂-UiO-66 as heterogeneous solid acid catalyst for biodiesel production. *Fuel* **2022**, *324*, 124537.
14. Abou-Elyazed, A.S.; Sun, Y.; El-Nahas, A.M.; Abdel-Azeim, S.; Sharara, T.Z.; Yousif, A.M. Solvent-free synthesis and characterization of Ca²⁺-doped UiO-66 (Zr) as heterogeneous catalyst for esterification of oleic acid with methanol: A joint experimental and computational study. *Mater. Today Sustain.* **2022**, *18*, 100110.
15. Li, H.; Han, Z.; Liu, F.; Li, G.; Guo, M.; Cui, P.; Yu, M. Esterification catalyzed by an efficient solid acid synthesized from PTSA and UiO-66 (Zr) for biodiesel production. *Faraday Discuss.* **2021**, *231*, 342–355.
16. Li, H.; Chu, H.; Ma, X.; Wang, G.; Liu, F.; Guo, M.; Yu, M. Efficient heterogeneous acid synthesis and stability enhancement of UiO-66 impregnated with ammonium sulfate for biodiesel production. *Chem. Eng. J.* **2021**, *408*, 127277.

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