engineering proceedings

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Proceeding Paper

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

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† Presented at the 4th International Electronic Conference on Applied Sciences, 27 October–10 November 2023; Available online: https://asec2023.sciforum.net/.

Abstract: Biodiesel is defined as a mixture of fatty acids and methyl esters. For esterification reaction in biodiesel production on acidic catalysts, waste cooking oils can be selected as raw material. Researchers generally use heterogeneous sulfonated solid catalysts for this reaction. However, the by-product water, the result of the biodiesel production process, absorbs on the catalyst surface. Therefore, 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 is known that UiO-66 has high chemical and thermal stability, high surface area, and uniform pore structure. The study aimed 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. The 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

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Citation: Ozcakir, G. Efficiency of Sulfonated UiO-66 on Biodiesel Production from Oleic Acid: An Optimization Study with ANCOVA. *Eng. Proc.* **2023**, *56*, 10. https://doi.org/10.3390/ASEC2023-15279

Academic Editor: Simeone Chianese

Published: 26 October 2023

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 consists of methyl esters. These methyl esters form as a result of a transesterification reaction between oils and methanol. As an oil source, edible and non-edible materials as well as waste cooking oils can used for biodiesel production. Using waste cooking oils as feedstock is preferred. In this way, waste management can be achieved. In addition, the feedstock is global, not a local product like rapeseed or palm oil, which means that transportation is not needed [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 (H_2SO_4), 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. In the dame way, 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].

In the 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 using 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 m^2/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. In addition, UiO-66 has resistance to high alkaline and acidic conditions. Utilization of sulfonated UiO-66 in biodiesel synthesis from oleic acid is a novel approach for the literature [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. As a result of the analyses, 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 of *p*-value; the effect of this variable on the oleic acid conversion rate was crucial. The obtained data for the computational study are 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 was applied to a 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, the 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. Using the ANCOVA analysis of sulfonated UiO-66, the R^2 was found to be 0.402. Figure 1 shows the possible oleic acid conversion ranges when it utilized a suitable amount of catalyst.

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	*p*-Value
Catalyst amount (wt.%)	5	1138.589	227.718	3.126	0.015
Temperature (°C)	1	174.536	174.536	2.396	0.128
Time (h)	1	807.785	807.785	11.088	0.002
Methanol/Oleic Acid Molar Ratio	1	909.085	909.085	12.479	<0.001
Residual	53	3861.085	72.851	--	--
Total	61	6457.242	105.856	--	--

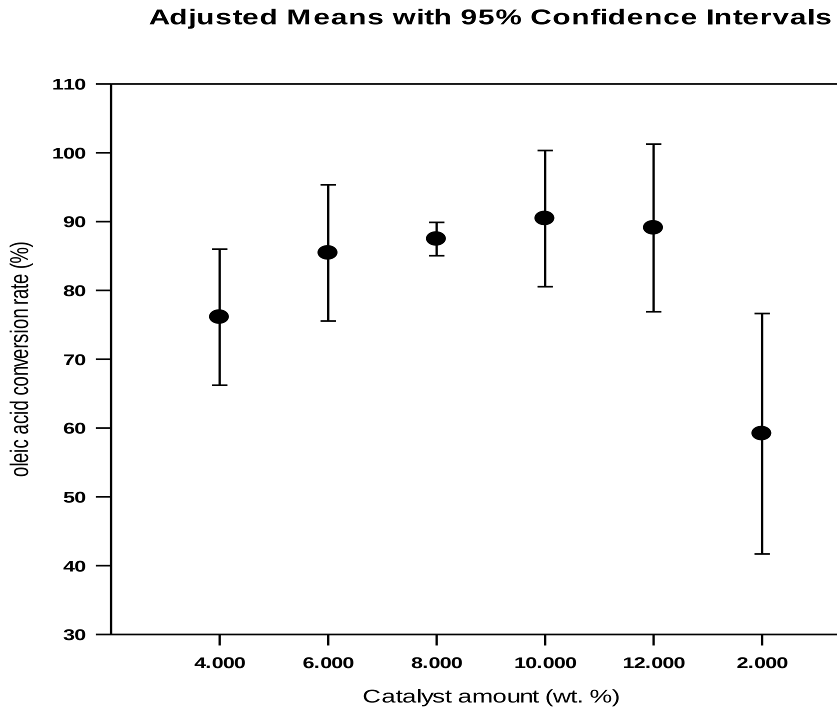

Figure 1. Adjusted means with 95% confidence intervals for sulfonated UiO-66.

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

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

Catalyst Amount (wt.%)	**Equations**
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 were obtained from the literature. Then, data were utilized in the analysis of covariance (ANCOVA). After that, the effective parameters in the experiments on the oleic acid conversion rate to biodiesel were revealed, the range of which can be used for the production of sulfonated UiO-66 catalyst and the equations which enabled the relationship between dependent and independent variables.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The author declares no conflict of interest.

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