Contents lists available at http://qu.edu.iq

Al-Qadisiyah Journal for Engineering Sciences

Journal homepage: https://qjes.qu.edu.iq

Hydrodeoxygenation of linoleic acid using water as hydrogen source on Co/HB zeolite

*Fouz Dhafer Yahia** and Ali A. Jazie* [iD]

Department of Chemical Engineering, College of Engineering, Al-Qadisiyah University, Al-Qadisiyah, Iraq.

ARTICLE INFO

ABSTRACT

Hydrodeoxygenation (HDO) is a critical step in upgrading biomass-derived feed-stocks to renewable fuels and valuable chemicals. Thus, we preserve the environment through the use of agricultural waste. Water plays the role of solvent, reactant, or byproduct in biomass HDO reactions catalyzed by Co/HB zeolite catalysts. The hydrodeoxygenation of linoleic acid was examined in this contribution in a patch-packed-bed reactor with a beta zeolite range of (5-15) mg catalyst at a temperature range of 230-300 K and throughout 2-3 h. Linoleic acid, an unsaturated fatty acid, was used in this work to create hydrocarbons in the diesel range, as well as to clarify the impacts of zeolite quantity, temperature, and time on the product yield to produce biofuels from Linoleic acid by hydrodeoxygenation in the high-pressure reactor in the presence of the catalyst, the products characterized by gas chromatography–mass spectrometry (GC-MS). Based on the results of optimization, it was determined that the hydrodeoxygenation reaction primarily eliminated the oxygen atoms from fatty acids. The yield of the intended products was 96.2% at the Co/HB zeolite amount (10% wt), high reaction temperature (270 ºC), and time (150 min) conditions.

1. Introduction

Due to biomass's greater productivity rate, a lot of work has recently been put into producing biofuels on a global scale [1]. Due to refinery output restrictions and excessive petroleum fuel use during the past ten years, crude oil prices have been steadily rising. Due to stringent environmental regulations, renewable energy is now a significant source of energy for many areas, particularly transportation. Due to its lower particulate matter and lower carbon dioxide emissions, biofuel is currently a preferred alternative energy source [2, 3]. Transesterifying vegetable oils yields biofuel, which was recently adopted for use in diesel engines. However, because the biofuel molecule contains oxygen atoms, it still has certain negative effects on diesel engines. That might have an impact on certain physical qualities, including high viscosity [4-6].

Currently, Direct usage of biofuel in modern diesel engines is not possible; it must first be blended with normal diesel. However, there are restrictions on how much biofuel can be blended with regular diesel. In order to produce hydrocarbons in the diesel range, vegetable oils must first undergo catalytic upgrading. It is anticipated that its qualities will be comparable to those of a traditional diesel, allowing for direct usage in a diesel engine [7, 8]. Generally, A variety of procedures, including pyrolysis, or thermal cracking, catalytic cracking, deoxygenation, and hydrodeoxygenation, can be used to produce biofuels like hydrocarbons from vegetable oils. While the diesel range of hydrocarbons can be preserved by deoxygenation, neither thermal nor catalytic cracking can produce a high yield in the diesel range [9]. An alternative to the hydrodeoxygenation (HDO) procedure is catalytic deoxygenation. The carbon resources present in the triglyceride

---

* *Corresponding author.*
   E-mail address: eng.chem21.post3@qu.edu.iq (Fouz Dhafer Yahia)

feedstock are partially lost during decarbonylation and decarboxylation, which both produce CO2 and CO. However, the majority of the carbon resources in the feedstock can be converted to hydrocarbons via hydrodeoxygenation, which produces H2O [10] . A form of hydrogenolysis known as HDO uses water to remove oxygen molecules from lipids [11]. Dupain et al. [12] under accurate FCC circumstances, rapseed vegetable oil's Co/HB zeolite cracking was examined. There were both gasoline and diesel-range hydrocarbon products. In the gasoline portion, they also recovered a significant amount of aromatics. Through decarbonylation, decarboxylation, and hydrogenation, triglycerides or fatty acids can be deoxygenated [13]. Using helium and low hydrogen partial pressure in a semi-batch reactor, Maki-Arvela et al. looked into the deoxygenation of stearic acid, ethyl stearate, and tristearine over a Pd/C catalyst [14] and Kubiková et al. [4]. They discovered that n-heptadecane was the major product produced from those reactants, which was mostly achieved by decarboxylating stearic acid and its derivatives. This investigation focused on the deoxygenation of linoleic acid, an unsaturated fatty acid, in a batch reactor with a Co/HB zeolite catalyst and water as a source of hydrogen. The goal of this research is to enhance the catalytic performance and product yields from the deoxygenation reaction.

2. Method and material

2.1. Material

Linoleic acid ($C_{18}H_{32}O_2$), (M.Wt. = 280.4 g/mol) and purity (99.8% from Chem-Lab NV (Zedelgem, Belgium), Alfa Aesar (Haverhill, Massachusetts, USA) produces a pure commercial H zeolite, Alfa Aesar additionally provides cobalt nitrate (Co (NO_3)$_2$.6H_2O) with a purity of 99.90%. (Haverhill, MA, USA)., Dichiorohexane ($C_6H_{12}Cl_2$), (M.Wt= 86.1 g/mol) and purity (98%) from Scharlau in Spain's Sentmenat.

2.2. Experiment

A high-pressure batch reactor with thick walls was used to conduct the reactions. To maintain a steady temperature while the gadget is in use a container with a capacity of 100ml is used. Science Avenue, High-tech District, Zhengzhou, China (as seen in Figs 1and 2) showed Schematic of Experimental Setup, A control circuit connected to the device to control the temperature, stirrer speed, and time). The reactor was equipped (100 ml batch reactor) for work, and it was cleaned with dichloromethane to remove all materials and dirt attached to the device. A (45 ml) of distilled water was added with (5 grams) of linoleic acid and a percentage of zeolite according to Table 3.

Figure 1. Photograph of experimental setup.

The device was placed at a temperature ranging between 230-300 degrees Celsius and remained in the reactor for a time of 2-3 hours, the device was left to cool down and extract the material from the reactor and put it in (Test Tube) and it is sent for Gas Chromotography-Mass Spectroscopy (GC-MS) examination.
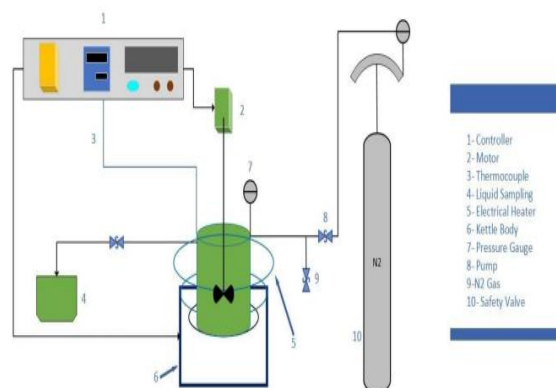

Figure 2. Schematic of experimental setup.

2.3. Preparation of catalysts

A commercial HB zeolite with a Si/Al ratio of 25 was calcined for 5 hours at 550 °C to serve as the support. Cobalt metal will be impregnated on the support using HB zeolite with different weight percentages, a modified version of the method was combined with a newly developed wetness approach. After being dissolved in 250 mL of deionized water, 1.55 g of H zeolite was mixed with 10 g of catalyst for 1 hour at room temperature. The resulting slurry was heated to 90 °C and stirred constantly until all of the water was gone and it had changed from a slurry to a paste. The paste was then dried at 110 °C in an oven for the entire following night, refined by calcining for three hours at 750 °C, and cooled to room temperature in a desiccator. Then, in order to use the catalysts later in this study, they were tightly packed and crushed with a crusher and pestle.

2.4. Experimental design

By hydrodeoxygenation processes using Co/HB zeolite, the Response Surface Method (RSM) is used to generate typical biofuel yield equations. Because of interaction effects between variables, it is not possible to optimize variables one at a time. RSM is a multivariable approach to optimizing experimental designs. The RSM is a mathematical instrument that can be used to design and analyze process variables that are unrelated to one another. Table 1 displays the experiment array suggested by Design expert-11 for the current work and obtained by Design expert-11 software program. Table 1 shows the process parameters with their specified levels. This study used the second-order model shown below, which was solved for using the least-squares method, to examine the relationship between the response and the independent variables [15].

Table 1. Process variables and the yield of biofuel.

Name	Code	Low (-1)	Middle (0)	High (+1)
Catalyst Ratio to Oil	A	5	10	15
Temperature	B	220	260	300
Time	C	0	120	180

Table 2. Design expert-11 software experimental design

Std	Run	Factor 1	Factor 2	Factor 3	Response 1
		A: Catalyst Ratio to Oil	B: Temperature	C: Time	yield%
		%	c	Min	
2	1	15	220	150	77.6
6	2	15	270	120	84.1
10	3	10	320	120	83.4
12	4	10	320	180	87.2
15	5	10	270	150	96
9	6	10	220	120	79.8
3	7	5	320	150	83.7
11	8	10	220	180	83.9
14	9	10	270	150	95.6
8	10	15	270	180	82.8
4	11	15	320	150	81.5
5	12	5	270	120	84.3
13	13	10	270	150	96.2
1	14	5	220	150	82.4
7	15	5	270	180	90.9

$$Y = a_0 + \sum a_0 x_i + \sum a_{ii} x_i 2 + \sum a_{ij} x_i x_j \qquad (1)$$

where Y is the output (Yield), i and j denote the pattern index numbers, a_0 denotes the intercept term, and $x_1, x_2,..., x_k$ denotes the process variables in coded form. The first order (linear) main effect, the second order main effect, and the interaction effect are denoted, respectively, by the letters a_i, a_{ii}, and a_{ij}. Following the completion of the analysis of variance, the model's suitability was examined by calculating the regression coefficient (R^2).

3. Results and discussion

3.1. Results of experimental design

Fifteen runs were carried out in accordance with Design expert-11 software design to look into the ideal circumstances for biodiesel production. The experimental findings involving actual Yield and predicted Yield are shown in Table 3. Results showed that efficiency of biofuel production was in the range of (77- 96). the precise effect of these parameters can be observed via ANOVA results. By using Design expert-11 software, results of biofuel production were analyzed and a quadratic model in term of real units of process parameters was formulated as Eq. 2.

The sequential sum of squares, lack of fit, and model summary statistic tests were used to determine which statistical model was the most acceptable by looking for the highest order, least significant lack of fit, and model that maximized the R^2 adj and R^2 pred values, respectively. The sequential sum

of squares, lack of fit, and model summary statistic tests were used to determine which statistical model was the most acceptable by looking for the highest order, least significant lack of fit, and model that maximized the R^2 adj and R^2 pred values, respectively.

Table 3. Experimental results of design expert-11 software design for biofuel production.

Run Order	Actual Value	Predicted Value	Residual	Leverage
1	77.6	77.23	0.375	0.75
2	84.1	83.94	0.1625	0.75
3	83.4	83.51	-0.1125	0.75
4	87.2	86.66	0.5375	0.75
5	96	95.93	0.0667	0.333
6	79.8	80.34	-0.5375	0.75
7	83.7	84.08	-0.375	0.75
8	83.9	83.79	0.1125	0.75
9	95.6	95.93	-0.3333	0.333
10	82.8	83.29	-0.4875	0.75
11	81.5	81.55	-0.05	0.75
12	84.3	83.81	0.4875	0.75
13	96.2	95.93	0.2667	0.333
14	82.4	82.35	0.05	0.75
15	90.9	91.06	-0.1625	0.75

$$\begin{aligned} yield\% = &95.93 - 1.91A + 1.51B + 1.65C \\ &+ 0.65AB - 1.98AC - 0.075BC \\ &- 6.34A^2 - 8.29B^2 - 4.07C^2 \end{aligned} \qquad (2)$$

These tests indicated that the quadratic model should be used instead of the aliased cubic model because it had the highest order, highest R^2, R^2 adj, and highest R^2 pred values among the other models, despite having a considerable lack of fit. Hence, the quadratic model was further evaluated by the ANOVA (Table 4) that confirmed its significance by its high F-value The Model F-value of 171.58 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A (catalyst amount), B (temperature), C (time), AC, A^2, B^2, C^2 are significant model terms.

Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve the model. The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

The Lack of Fit F-value of 5.06 implies the Lack of Fit is not significant relative to the pure error. There is a 16.94% chance that a Lack of Fit F-value as showed in Table 4

Table 4. ANOVA results for the quadratic model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	495.43	9	55.05	171.58	< 0.0001	significant
A-Catalyst Ratio to Oil	29.26	1	29.26	91.2	0.0002	
B-Temp.	18.3	1	18.3	57.04	0.0006	
C-Time	21.78	1	21.78	67.89	0.0004	
AB	1.69	1	1.69	5.27	0.0702	
AC	15.6	1	15.6	48.63	0.0009	
BC	0.0225	1	0.0225	0.0701	0.8017	
A²	148.49	1	148.49	462.83	< 0.0001	
B²	253.85	1	253.85	791.23	< 0.0001	
C²	61.06	1	61.06	190.32	< 0.0001	
Residual	1.6	5	0.3208			
Lack of Fit	1.42	3	0.4725	5.06	0.1694	not significant
Pure Error	0.1867	2	0.0933			
Cor Total	497.04	14				

The Adjusted R^2 of 0.9910 and the Predicted R^2 of 0.9535 are reasonably in agreement; hence, the difference is less than 0.2. The ratio of signal to noise is measured by Adeq Precision. A ratio of at least 4 is preferred. To move around the design space, utilize this model.
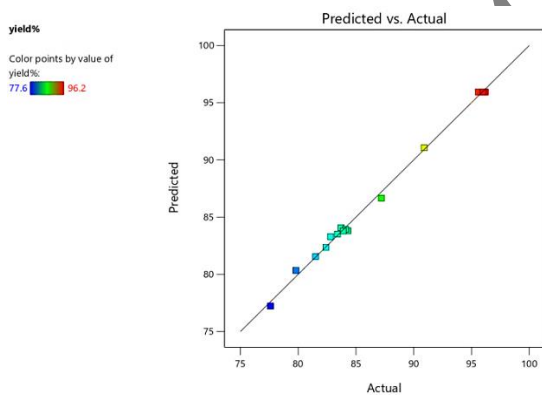

Figure 3. Yield biodiesel experimental data versus expected data

3.2. Effect of process variables on the yield

RSM graphics can be used to show the interaction impacts of the chosen variables and how they affect the response. According to the hierarchical quadratic model, Figure 4a depicts the response surface and contour plots for biofuel content from the deoxygenation of linoleic acid as a function of catalyst loading and reaction time while maintaining the reaction temperature constant at their medium levels (276.47 oC). As shown in

Figure 4a, the biofuel produced by the hydrodeoxygenation of linoleic acid increases as the reaction proceeds independently of the catalyst loading while it decreases as the catalyst loading is increased after reaching a maximum at about 10% of the oil weight. A poor relationship between the catalyst loading and the reaction time can be seen in the contour plot of Figure 4b. Additionally, it is clear that a biofuel content from the hydrodeoxygenation of linoleic acid that is higher than the 96.2% limit value can be achieved for a wide range of catalyst loading and reaction times, or for different combinations of both. Additionally, the software in use proposed a number of permutations of the process factors that would yield the desired actual maximum biofuel from the deoxygenation of linoleic acid content of 96.2%, as shown in Table 2 contrary to the current study, the yield of generated methyl esters was reduced when the reaction duration increased beyond a particular point [16, 17, 18].

While Betiku et al. [19] found a decrease in the yield of neem seed oil methyl esters with an increase in the catalyst loading and the reaction duration over specific values, other studies have found a similar favorable effect of the catalyst loading on the Ceiba pentandra oil methyl esters production. Evaluated a variety of operating circumstances. discovered a strong interaction between the two variables when the yield of yellow oleander oil methyl esters increased continuously as reaction duration and catalyst loading increased [15]. Additionally, independent of the amount of catalyst used, a high palm kernel oil methyl ester production was recorded at a protracted reaction time [16].

a

b
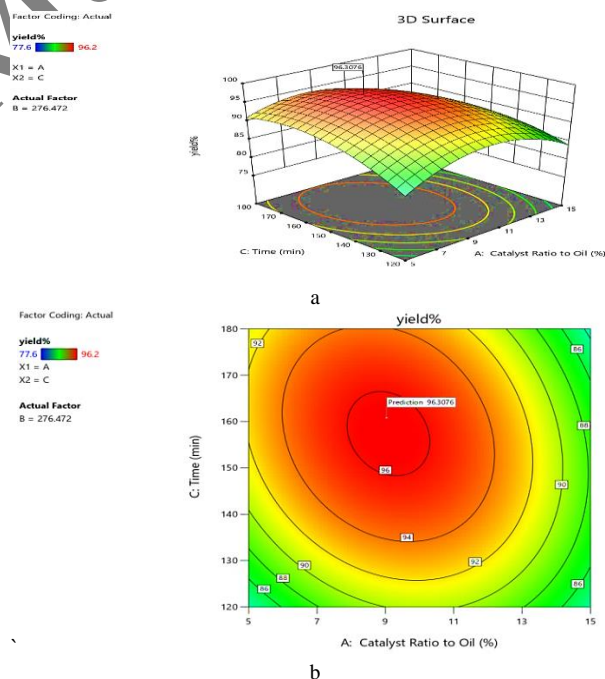
Figure 4. The response surface (a) and contour (b) plots for the biofuel content as a function of catalyst loading and reaction time according to the hierarchical quadratic model at constant temperature

The impact of the catalyst is depicted in Figures 5a and b. ratio to oil on the Yield for various values of temperature (220-300) at constant time (160.798). Figure 5a represents the response surface plot while figure 5b

shows the corresponding contour plot. The shape of control plot indicates the nature and extent of the interaction. From the surface plot, it was observed that, at temperature (300), an increase in Yield occurs as the catalyst ratio from (5-15). The corresponding contour plot confirms that value of the Yield ≥ 95% lies in a small area in which the temperature ranged between (300-320) and catalyst range of (7.3-14.5).
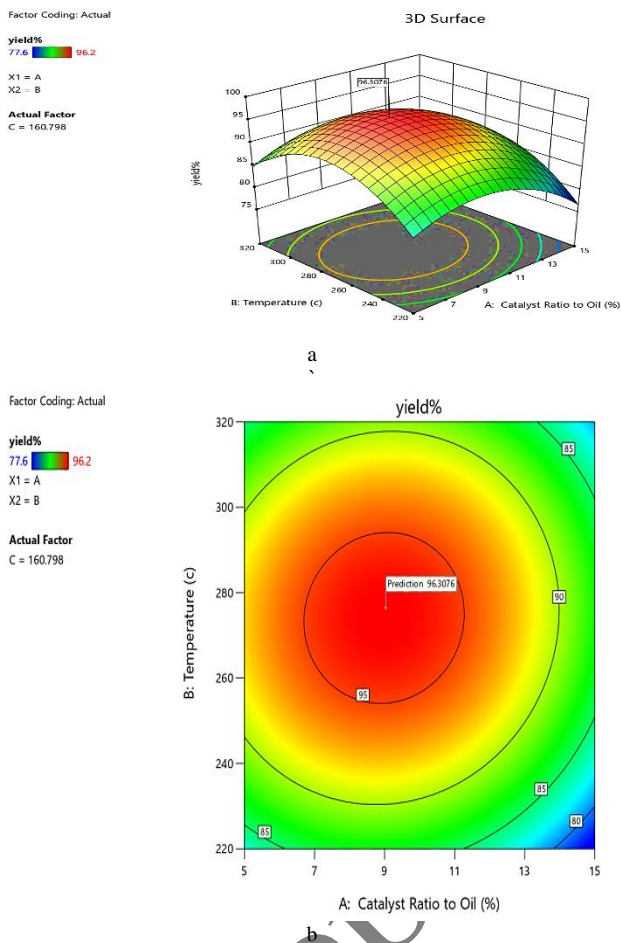

Figure 5. Shows how the response surface plot (a) and contour plot (b) for the Yield are affected by the catalyst ratio to oil and temperature.

Figures 6a, b depict the relationship between temperature and yield for different time values (120-180 min) and a constant catalyst to oil ratio (9.003). The response surface plot is shown in Figure 6a, and the matching contour plot is shown in Figure 6b. The size and type of the interaction are revealed by the control plot's form. It was seen from the surface plot that at temperature (300), Yield increases as the time increases from (120-180 min). The preceding contour map demonstrates that the Yield value of 96.2% was found to be concentrated in a limited area with temperatures between (270-300) and time between (150-180) minutes.
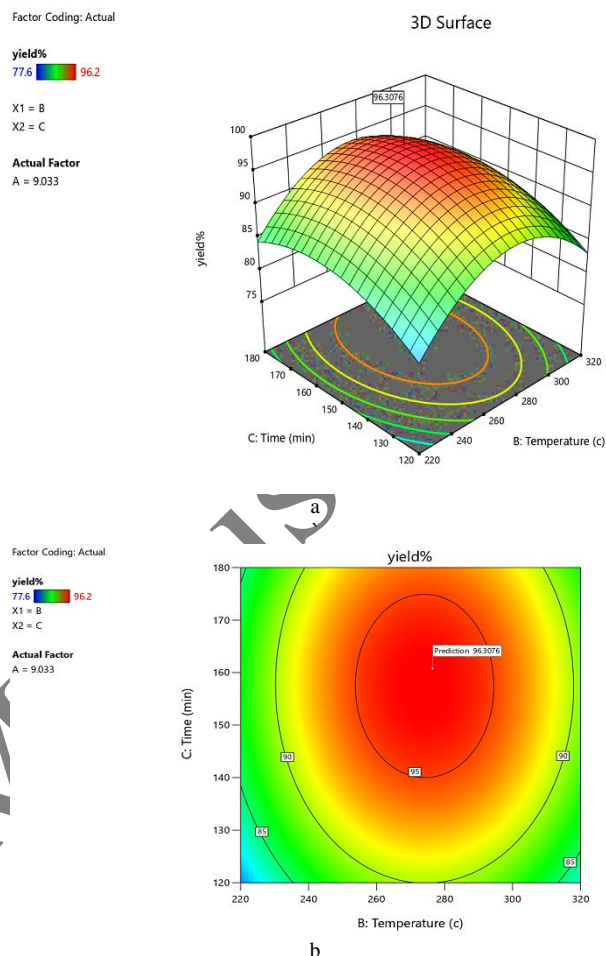

Figure 6. Impact of temperature and time on the Yield as represented by the response surface plot (b) and contour plot.

4. Conclusion

Lenoliec acid is hydrodeoxygenated in this work to produce energy from biomass utilizing water as the source of hydrogen and Co/HB zeolite as the catalyst. The process is improved using response surface methodology (RSM). The fact that the models and the results of the experiments agreed well demonstrates that the methodology in question is beneficial to the process of optimization. It was found that the best results came from setting the Catalyst Ratio to Oil to 10%, the temperature to 270 ºC, the time to 150 minutes, and the actual maximum biofuel yield from the deoxygenation of linoleic acid was 96.2%.
.

Authors' contribution

All authors contributed equally to the preparation of this article.

Declaration of competing interest

The authors declare no conflicts of interest.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

[1] A.A. Jazie, J. Haydary, S.A. Abed, M.F. Al-Dawody, Hydrothermal liquefaction of Fucus vesiculosus algae catalyzed by Hβ zeolite catalyst for Biocrude oil production, Algal Research, 61 (2022) 102596. https://doi.org/10.1016/j.algal.2021.102596

[2] N. Martini, J.S. Schell, Plant oils as fuels: present state of science and future developments, Springer Science & Business Media, Berlin, Heidelberg, 2012. https://doi.org/10.1007/978-3-642-72269-1

[3] A. Monyem, J.H. Van Gerpen, The effect of biodiesel oxidation on engine performance and emissions, Biomass bioenergy, 20 (2001) 317-325.

[4] I. Kubičková, M. Snåre, K. Eränen, P. Mäki-Arvela, and D. Y. Murzin, Hydrocarbons for diesel fuel via decarboxylation of vegetable oils, Catalysis Today, 106 (2005) 197-200. https://doi.org/10.1016/j.cattod.2005.07.188

[5] O. Şenol, T.-R. Viljava, and A. Krause, Effect of sulphiding agents on the hydrodeoxygenation of aliphatic esters on sulphided catalysts, Applied Catalysis A: General, 326 (2007) 236-244. https://doi.org/10.1016/j.apcata.2007.04.022

[6] R. Altın, S. Cetinkaya, and H.S. Yücesu, The potential of using vegetable oil fuels as fuel for diesel engines, Energy conversion management, 42 (2001) 529-538. https://doi.org/10.1016/S0196-8904(00)00080-7

[7] J. Gusmao, D. Brodzki, and G. Djéga-Mariadassou, and R. Frety, Utilization of vegetable oils as an alternative source for diesel-type fuel: hydrocracking on reduced Ni/SiO2 and sulphided Ni-Mo/γ-Al2O3, Catalysis Today, 5 (1989) 533-544. https://doi.org/10.1016/0920-5861(89)80017-3

[8] P. Nunes, D. Brodzki, G. Bugli, and G. Djéga-Mariadassou, Hydrocracking of soybean oil under pressure: research procedure and general aspects of the reaction, Revue De L Institut Francais Du Petrole, 41 (1986) 421-431.

[9] K. Maher, D. Bressler, Pyrolysis of triglyceride materials for the production of renewable fuels and chemicals, Bioresource technology, 98 (2007) 2351-2368. https://doi.org/10.1016/j.biortech.2006.10.025

[10] M.J. Nuhma, H. Alias, M. Tahir, and A.A. Jazie, Bimetallic Lanthanum-Cerium-Loaded HZSM-5 Composite for Catalytic Deoxygenation of Microalgae-Hydrolyzed Oil into Green Hydrocarbon Fuels, Molecules, 27 (2022) 8018. https://doi.org/10.3390/molecules27228018

[11] M.J. Nuhma, H. Alias, and M. Tahir, A.A. Jazie, Ce-Loaded HZSM-5 Composite for Catalytic Deoxygenation of Algal Hydrolyzed Oil into Hydrocarbons and Oxygenated Compounds, Molecules, 27 (2022) 7251. https://doi.org/10.3390/molecules27217251

[12] X. Dupain, D.J. Costa, C.J. Schaverien, M. Makkee, and J.A. Moulijn, Cracking of a rapeseed vegetable oil under realistic FCC conditions, Applied Catalysis B: Environmental, 72 (2007) 44-61. https://doi.org/10.1016/j.apcatb.2006.10.005

[13] M. Snare, I. Kubickova, P. Maki-Arvela, K. Eranen, and D.Y. Murzin, Heterogeneous catalytic deoxygenation of stearic acid for production of biodiesel, Industrial Engineering Chemistry Research, 45 (2006) 5708-5715. https://doi.org/10.1021/ie060334i

[14] P. Mäki-Arvela, I. Kubickova, M. Snåre, K. Eränen, and D.Y. Murzin, Catalytic deoxygenation of fatty acids and their derivatives, Energy Fuels, 21 (2007) 30-41. https://doi.org/10.1021/ef060455v

[15] M.A. Bezerra, R.E. Santelli, E.P. Oliveira, L.S. Villar, L.A. Escaleira, Response surface methodology (RSM) as a tool for optimization in analytical chemistry, Talanta, 76 (2008) 965-977. https://doi.org/10.1016/j.talanta.2008.05.019

[16] V.O. Odude, A.J. Adesina, O.O. Oyetunde, O.O. Adeyemi, N.B. Ishola, A.O. Etim, and E. Betiku, Application of agricultural waste-based catalysts to transesterification of esterified palm kernel oil into biodiesel: A case of banana fruit peel versus cocoa pod husk, Waste biomass valorization, 10 (2019) 877-888. https://doi.org/10.1007/s12649-017-0152-2

[17] E. Betiku, A.M. Akintunde, T.V. Ojumu, Banana peels as a biobase catalyst for fatty acid methyl esters production using Napoleon's plume (Bauhinia monandra) seed oil: A process parameters optimization study, Energy, 103 (2016) 797-806. https://doi.org/10.1016/j.energy.2016.02.138

[18] M. Balajii, S. Niju, A novel biobased heterogeneous catalyst derived from Musa acuminata peduncle for biodiesel production–Process optimization using central composite design, Energy Conversion Management, 189 (2019) 118-131. https://doi.org/10.1016/j.enconman.2019.03.085

[19] E. Betiku, A.O. Etim, O. Pereao, T.V. Ojumu, Two-step conversion of neem (Azadirachta indica) seed oil into fatty methyl esters using a heterogeneous biomass-based catalyst: An example of cocoa pod husk, Energy Fuels, 31 (2017) 6182-6193. https://doi.org/10.1021/acs.energyfuels.7b00604