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

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ABSTRACT

Hydrodeoxygenation (HDO) is a critical step in upgrading biomass-derived feedstock to renewable fuels and valuable chemicals. Thus, preserving the environment through the use of agricultural waste. Water plays the role of solvent, reactant, or byproduct in biomass HDO reactions, which are catalyzed by Co/HB zeolite catalysts. In this investigation, The hydrodeoxygenation of linoleic acid was examined in a patch-packed-bed reactor with a beta zeolite range of (5-15) mg and catalyzed at a temperature range of 230-300 K for 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 impact of zeolite quantity, temperature, and time on the yielded product, to produce biofuels from Linoleic acid by hydrodeoxygenation in the high-pressure reactor in the presence of the catalyst. The products are then characterized by gas chromatography-mass spectrometry (GC-MS). Based on the optimization results, 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 °C), and time (150 min) conditions.

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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]. Trans-esterifying vegetable oils yield 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, 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 feedstock are partially lost during decarbonization 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].

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Nomenclature:

Y	Output field
a_{ij}	Intercept terms
x_{ij}	Process variables
R	Regression coefficient

Subscripts

I and j	Index notation
A, B, C	Constants

A form of hydrogenolysis known as HDO uses water to remove oxygen molecules from lipids [11]. Dupain et al. [12] under accurate FCC circumstances, rapeseed 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 number of aromatics. Through decarbonization, 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. investigated the deoxygenation of stearic acid, ethyl stearate, and tristearin 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 ($Co(NO_3)_2 \cdot 6H_2O$) with a purity of 99.90%. (Haverhill, MA, USA)., Dichlorohexane ($C_6H_{12}Cl_2$), (M.Wt= 86.1 g/mol) and purity (98%) from Scharlau in Spain's Sentiment.

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 100 (ml) is used. Science Avenue, High-tech District, Zhengzhou, China, as seen in Figs 1 and 2, showed a schematic of the experimental setup. A control circuit connected to the device to control the temperature, stirrer speed, and time). The reactor was equipped with a 100 (ml) batch reactor for work, and it was cleaned with dichloromethane to remove all materials and dirt attached to the device. 45 (ml) of distilled water was added with 5 (grams) of linoleic acid and a percentage of zeolite according to Table 3. 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 in a test tube and it is sent for Gas Chromatography-Mass spectroscopy (GC-MS) examination.

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.

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, to use the catalysts later in this study, they were tightly packed and crushed with a crusher and pestle.



Figure 1. Photograph of the experimental setup.

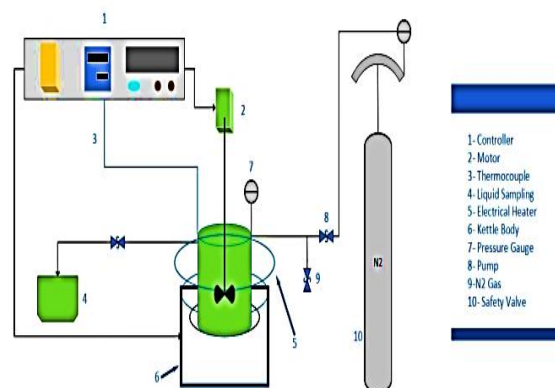


Figure 2. Schematic of the experimental setup.

2.3. 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 the 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 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	005	010	015
Temperature	B	220	260	300
Time	C	000	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	
02	01	15	220	150	77.6
06	02	15	270	120	84.1
01	03	10	320	120	83.4
02	04	10	320	180	87.2
01	05	10	270	150	96.0
09	06	10	220	120	79.8
03	07	05	320	150	83.7
01	08	10	220	180	83.9
01	09	10	270	150	95.6
08	10	15	270	180	82.8
04	11	15	320	150	81.5
05	12	05	270	120	84.3
01	13	10	270	150	96.2
01	14	05	220	150	82.4
07	15	05	270	180	90.9

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

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, \dots, 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

The results from this experimental setup are listed as follows:

3.1. Results of experimental design

Fifteen runs were carried out in accordance with Design expert-11 software design to investigate the ideal circumstances for biodiesel production. The experimental findings involving actual Yield and predicted Yield are shown in Table 3. Results showed that the 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, the results of biofuel production were analyzed and a quadratic model in terms 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
01	77.6	77.23	+0.3750	0.750
02	84.1	83.94	+0.1625	0.750
03	83.4	83.51	-0.1125	0.750
04	87.2	86.66	+0.5375	0.750
05	96.0	95.93	+0.0667	0.333
06	79.8	80.34	-0.5375	0.750
07	83.7	84.08	-0.3750	0.750
08	83.9	83.79	+0.1125	0.750
09	95.6	95.93	-0.3333	0.333
10	82.8	83.29	-0.4875	0.750
11	81.5	81.55	-0.0500	0.750
12	84.3	83.81	+0.4875	0.750
13	96.2	95.93	+0.2667	0.333
14	82.4	82.35	+0.0500	0.750
15	90.9	91.06	-0.1625	0.750

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

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 the 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, confirming 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 an 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 shown in Table 4. The Adjusted $R^2 \cong 0.99$ and the predicted $R^2 \cong 0.95$ are reasonably in agreement. Hence, the difference is less than 0.2. The ratio of signal to noise is measured by Adeq Precision. Thus, a ratio of at least 4 is preferred. To move around the design space, utilize this model. 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 the 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, 20].

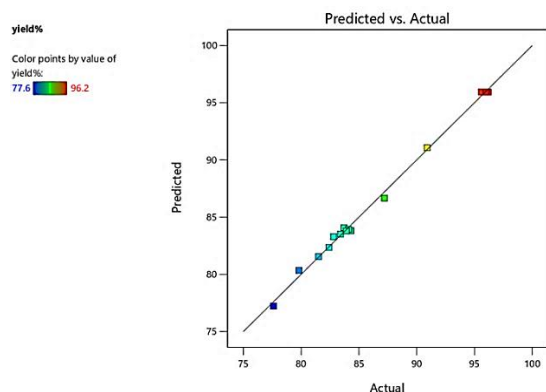


Figure 3. Yield biodiesel experimental data versus expected data

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 °C).

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 Fig. 5b shows the corresponding contour plot. The shape of the 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 the value of the Yield \geq 95% lies in a small area in which the temperature ranges between (300-320) and the catalyst range of (7.3-14.5). Fig. 6a, b

depicts 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.

Table 4. ANOVA results for the quadratic model

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	495.43	09	55.05	171.58	< 0.0001S
A- Catalyst to Oil	029.26	01	29.260	91.200	0.0002
B-Temp.	018.30	01	18.300	57.040	0.0006
C-Time	021.78	01	21.780	67.890	0.0004
AB	001.69	01	01.690	05.270	0.0702
AC	015.60	01	15.600	48.630	0.0009
BC	0.0225	01	0.0225	0.0701	0.8017
A ²	148.49	01	148.49	462.83	< 0.0001
B ²	253.85	01	253.85	791.23	< 0.0001
C ²	061.06	01	61.060	190.32	< 0.0001
Residual	001.60	05	0.3208	-----	-----
Lack of Fit	001.42	03	0.4725	05.060	0.1694NS
Pure Error	0.1867	02	0.0933	-----	-----
Cor Total	497.04	14	-----	-----	-----

S: Significant; NS: Not significant

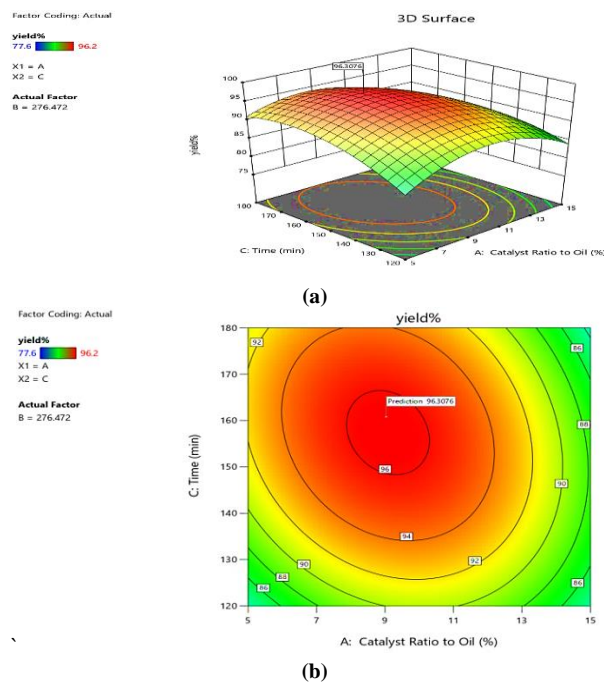
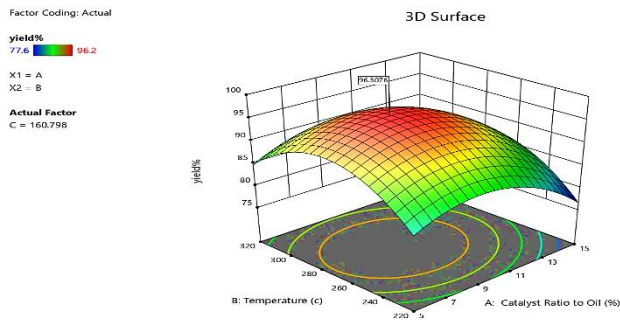
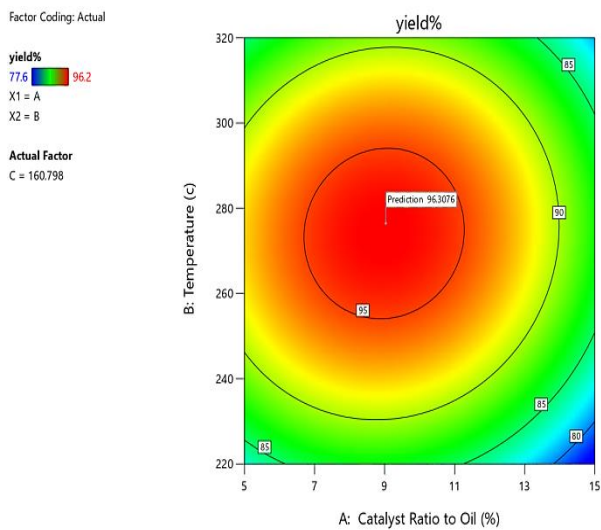


Figure 4. The response surface (a) and contour (b) plots for the biofuel content as a function of catalyst loading and reaction time according to the hierarchical quadratic model at constant temperature

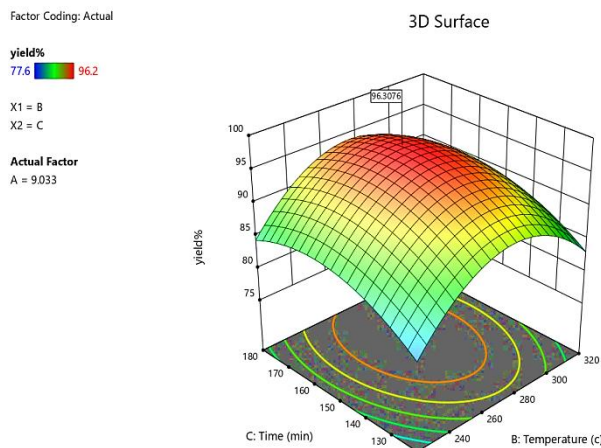


(a)

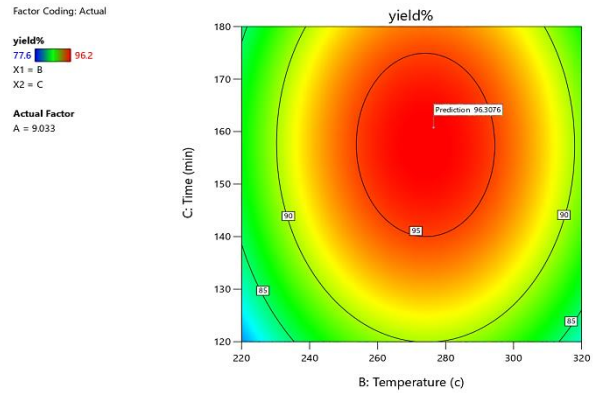


(b)

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.



(a)



(b)

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

4. Conclusion

Linoleic acid was Hydrodeoxygenated in this work to produce energy, with biomass utilizing water as the source of hydrogen and Co/HB zeolite as the catalyst. This process is improved using response surface methodology (RSM). The fact that the models and the results of the experiments agree well demonstrates that the methodology in question is beneficial for the optimization process. It was found that the best results came from setting the Catalyst Ratio to Oil at 10%, the temperature at 270 °C, the time at 150 minutes, and the maximum biofuel yielded 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.

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Data availability

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

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