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Response Surface-Optimized Isolation of Essential Fatty Acids via Castor Oil Dehydration

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ABSTRACT. The reaction conditions optimization, including the temperature of the reaction, amount of catalyst required, and reaction time for the linoleic acids (LAs) and conjugated linoleic acids (CLAs) production by catalytic dehydration of castor oil via saponification was investigated by response surface methodology (RSM). It was confirmed that all three parameters (temperature, time, and amount of catalyst) were influential factors in isolating LAs and CLAs. When the temperature was increased, the iodine value increased, and the reaction time and catalyst amount increased. The optimal reaction conditions were: 240 ℃, 2.2 h reaction time, and 7 wt% catalyst amount. The maximum iodine value reached 156.25 with 91.69% conversion to the essential fatty acids.

Key words: Castor oil, Dehydration, Response surface methodology (RSM)

INTRODUCTION

Castor (Ricinus communis L) is a native of tropical Asian countries, including Indonesia. Castor seeds are pressed and extracted into castor oil to manufacture coatings, soaps, lubricants, and other chemical industries. The critical component of castor oil is ricinoleic acid (12-hydroxy-9-octadecenoic acid). The high content of ricinoleic acid (86-90%) makes it potential for medicinal use as well.[1–3] The hydroxyl group of ricinoleic acid can be dehydrated to form new double bonds called conjugated linoleic acid (CLAs) and linoleic acid (LAs). This process is generally carried out at 250 ℃ in the presence of the catalyst under vacuum.[4,5]

Dehydration of castor oil into CLAs and LAs is worth attention since castor oil is relatively cheaper than other essential oils and is a simple starting material. The use of catalysts such as mineral acids, salts, clays, resin, and oxides was reported.[6,7] Heterogeneous catalysts are preferable due to their advantages, such as being easy to separate, reusable and recyclable. Among heterogeneous catalysts, sodium bisulfate is a potentially effective catalyst for the dehydration of castor oil. However, sodium bisulfate can be mixed easily, making it difficult to separate, and its specific surface area is small. Based on these disadvantages, silica and alumina-based catalysts were tested.[8–12]

Despite many studies on castor oil dehydration and development, the response surface methodology (RSM) using γ-alumina as a catalyst has not been investigated. This study aimed to optimize the reaction parameters, i.e. dehydration reaction time, reaction temperature, and amount of γ-alumina catalyst to obtain the maximum conversion of ricinoleic acid from castor oil to CLAs and LAs.

METHODOLOGY

Materials

Castor oil was purchased from a local company (PT. Darjeeling Sembrani Aroma, Indonesia). All solvents/

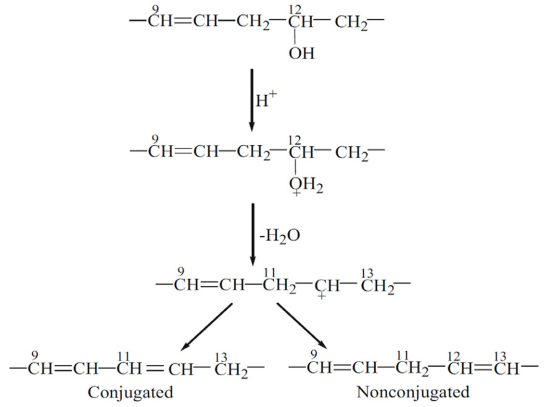

***Figure* 1.** Acid-catalyzed mechanism of dehydration of castor oil.[13]

chemicals, including pure LCAs and LAs for standard and γ-Al_2O_3 used, were of analytical grade and obtained from Merck (Darmstadt, Germany).

Catalytic Dehydration of Ricinoleic Acid

Ricinoleic acid was obtained by saponification of castor oil as follows: 200 g of castor oil was diluted in the KOH-ethanol solution while heating at 68 ℃ for two h. The product mixture was cooled and neutralized in the 5 M HCl solution while stirring for two h. The mixture was then put in the dropping funnel overnight to separate ricinoleic acid from the mixture. The ricinoleic acid (upper layer) was collected for dehydration reaction. The desired amount of ricinoleic acid was added to a three-neck flask, followed by γ-Al_2O_3 as a catalyst at the designated temperatures. Nitrogen gas was blown inside the flask for a few minutes to remove the residual air before starting the reaction. After the reaction, the product was separated from the catalyst, and the iodine value was calculated as follows according to the Wijs method:[12]

$$W = \frac{12.69 \times c \times (V_1 - V_2)}{m} \quad (1)$$

W = iodine value of the sample, g (I_2)/100 g
c = concentration of sodium thiosulfate standard solution, mol/L
V_1 = volume of the standard solution that was consumed by the blank solution, mL
V_2 = sample solution, mL
m = mass of sample, g

The fatty acid components of the optimal iodine value was then further determined by high-performance liquid chromatography (HPLC).

RSM Experimental Design

RSM was applied to determine the reaction conditions for maximum conversion of ricinoleic acid of castor oil after varying one independent variable at a time while keeping the others constant, i.e., reaction temperature, reaction time, and amount of catalyst. An independent variable with an appropriate range was determined for RSM. A three-variable and three levels D-optimal design was adopted from the dehydration reaction to optimise the reaction conditions for maximum conversion. To evaluate the experimental design, the program Minitab 20 was used. Reaction temperature (X1: 175, 200, 225 ℃), reaction time (X2: 2, 3, 4 h), and amount of catalyst (X3: 3, 7, 11 wt.%) were checked as variables. The design of the experiment consists of 18 experiments of three variables, each at three levels (–1, 0, +1).[14]

RESULTS AND DISCUSSION

Design of Experiments and Factor Levels Selection

In this study, the reaction temperature was selected at 175, 200, and 225 ℃ since higher temperatures may lead to the polymerization of ricinoleic acid. 2, 3 and 4 h were chosen as the lower to upper points of reaction time, and for the γ-Al_2O_3 content, 3, 7, and 11 wt.% were selected. As shown in *Fig*. 2, the iodine value tends to increase with the increase of reaction time and then to decrease where the maximum iodine value was reached in 2.2 h reaction

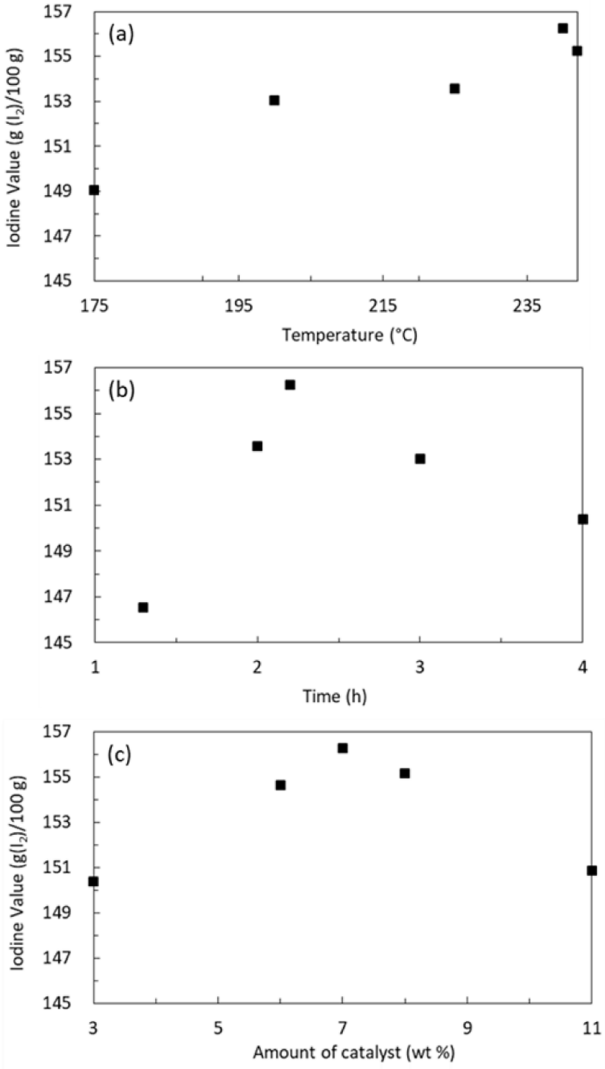

***Figure* 2.** Experimental results of three variables (a) temperature (b) reaction time (c) amount of catalyst (wt.%).

***Table* 1.** Analysis of variance results, regression coefficients and, P-value

Source	Sum of squares	Degree of freedom	Mean square	F-value	P-value
Model	298.261	9	33.140	1.92	0.162
Residual Error	172.662	10	17.266		
Lack-of-fit	140.301	5	28.060	4.34	0.067
Pure error	32.362	5	6.472		
Total	470.923	19			
Variables		Regression coefficient			P-value
Intercept		89.35			0
X_1		3.16			0.01
X_2		– 0.62			0.546
X_3		– 0.38			0.711

time. A similar trend was observed for the amount of catalyst. The maximum iodine value was obtained at 7 wt.%.

Model Fitting

The experimental runs were set to 1–20, and the iodine value was obtained. The response surface was created based on the data obtained from the above design and was fitted to the second-order polynomial equation. The independents variables coefficients determined for the linear polynomial model for the iodine value of the dehydrated ricinoleic acid are given in Eq. 2:

$$\text{Iodine Value} = 26.6 + 0.946X_1 + 7.3X_2 + 1.86X_3 - 0.00194X_1^2 - 0.78X_2^2 - 0.1638X_3^2 - 0.0148X_1X_2 + 0.0025X_1X_3 - 0.057X_2X_3 \quad (2)$$

The agreement of the models with the data was found at 99% probability, with the R2 (R-squared) percentage being 63.34%. The regression model shown in the analysis of variance (*Table* 1) was statistically good and had no significant ($p > 0.05$) lack of fit.

Parameters Effect on Ricinoleic Acid Dehydration

Table 1 showed that the most significant effect on the dehydration of ricinoleic acid was a linear term of the temperature followed by reaction time and the amount of catalyst.

Temperature. The dehydration temperature is essential since it is an endothermic reaction. It shows that temperature has a positive linear effect by increasing from 175 ℃ to 240 ℃, represented by the iodine value. The iodine value increases monotonically from 149.06 to 156.25 as the reaction temperature increases. Above 240 ℃ (242 ℃) iodine value was decreased to 155 due to the side reaction appearance, such as thermal polymerization, thermal cracking, formation of coke, etc., that may happen at higher temperatures.[13] Therefore, 240 ℃ is the best reaction temperature for ricinoleic acid dehydration.

Reaction time. The reaction time has a p-value of more than 0.05 (*Table* 1), which indicates that reaction time had a positive linear effect on the conversion of ricinoleic acid. A slight increase in iodine value was observed at the increase of reaction time from 1 to 2 h. Further increment of reaction time resulted in decreasing in iodine value.[15] This might be because the polymerization of ricinoleic acid is preferable than the dehydration to occur at the longer reaction time.[16,17]

Amount of catalyst. Similar to the reaction time, the amount of catalyst had a positive linear effect towards the dehydration reaction. It was increasing γ-Al_2O_3 content from 3 wt.% to 7 wt.% enhanced the iodine value from 139 to 156—however, more than 7 wt.% amount of catalyst lowered the iodine value and led to the undesirable dark product.[14] Therefore, in this work, 7 wt.% amount of catalyst is the most appropriate.

Optimization of Ricinoleic Conversion

Two of the three independent variables are plotted in the response surface and can be observed in *Fig.* 3. *Fig.* 3a denotes the surface plot of the iodine value as a function of temperature and reaction time at a catalyst amount of 7 wt.%. At 240 ℃, the iodine value increased along with reaction time (*Fig.* 3b). A similar trend was obtained for the amount of the catalyst (*Fig.* 3c). It is clearly shown that all three independent variables had a positive and significant effect on the conversion of ricinoleic acid, as represented by the iodine value. The increasing iodine value from 88.50 (initial castor oil iodine value according to the calculation) to 156.25 confirms that RSM method is a suitable method to determine the best reaction condition with γ-Al_2O_3 as a catalyst. The maximum obtained iodine value was 156.25,

***Table* 2.** HPLC information of (un)dehydrated castor oil

Name	Linoleic acid (%)	Conjugated linoleic acid (%)	Ricinoleic Acid (%)
Undehydrated castor oil	5.8	-	89.15
Dehydrated castor oil	91.56	0.13	8.31

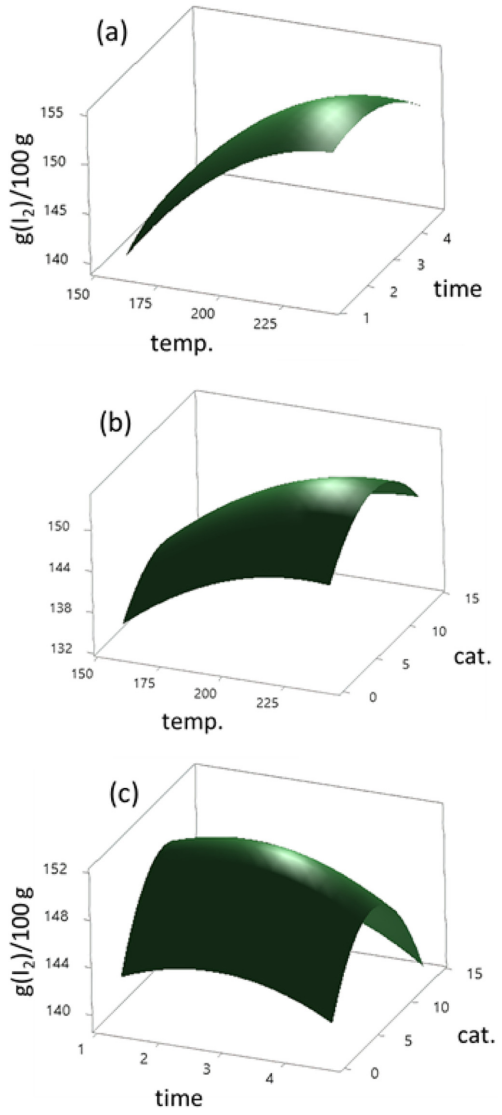

***Figure* 3.** Response surface plot (a) effect of temperature and time at the center level of catalyst, (b) effect of temperature and amount of catalyst at the center level of time, (c) effect of time and amount of catalyst at center of temperature on the iodine value per 100 g.

produced at 240 ℃ for 2.2 h of reaction with 7wt.% catalyst. The conversion of ricinoleic acid into linoleic acid and conjugated linoleic acids were 91.56% and 0.13%, respectively (*Table* 2).

CONCLUSION

An efficient method was designed to obtain linoleic and conjugated linoleic acid from castor oil. Dehydration of ricinoleic acid via saponification of castor oil effectively converts ricinoleic acid into linoleic and conjugated linoleic acid. In this study, γ-Al_2O_3 was used as a catalyst to optimize the conversion of ricinoleic acid. The results show that after dehydration, 91.56% linoleic acid and 0.13% conjugated linoleic acid was obtained with a 156.25 iodine value. The optimum reaction conditions were: at 240 ℃ for 2.2 h with 7 wt.% of catalyst. All three parameters significantly affect the production of linoleic and conjugated linoleic acid from castor oil.

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Supporting Information. HPLC and ^{1}H-NMR of the dehydrated ricinoleic acid are available in the online version of this article.

REFERENCES

1. Chauke, N. P.; Mukaya, H. E.; Nkazi, D. B. *Sci. Prog.* **2019**, *102*, 199.
2. Nitbani, F. O.; Tjitda, P. J. P.; Wogo, H. E.; Detha, A. I. R. *J. Oleo Sci.* **2022**, *71*, 781.
3. Naik, S. N.; Saxena, D. K.; Dole, B. R.; Khare, S. K. *Potential and Perspective of Castor Biorefinery*. Elsevier B.V., 2018.
4. Mutlu, H.; Meier, M. A. R. *Eur. J. Lipid Sci. Technol.* **2010**, *112*, 10.
5. Prasad, R. B. N.; Rao, B. V. S. K. *Chemical Derivatization of Castor Oil and Their Industrial Utilization*. Elsevier Inc., 2017.
6. Ogunniyi, D. S. *Bioresour. Technol.* **2006**, *97*, 1086.
7. Yang, L.; Huang, Y.; Wang, H. Q.; Chen, Z. Y. *Chem. Phys. Lipids* **2002**, *119*, 23.
8. Ding, J. F. *et al.*, *Chem. Eng. Technol.* **2018**, *41*, 2186.
9. Mamudu, A. O.; Charles, E. A.; Elehinafe, F.; Odunlami, O.; Akinneye, D. *Int. J. Mech. Eng. Technol.* **2019**, *10*, 353.
10. Orozco, L. M.; Cardona, S.; Gomez, C.; Inciarte, H.; Vil-

lada, Y.; Rios, L. *Prog. Org. Coatings* **2021**, *161*, 106467.
11. Guner, F. S., *JAOCS J. Am. Oil Chem. Soc.* **1997**, *74*, 409.
12. Yan, C. X. *et al.*, *Zeitschrift fur Anorg. und Allg. Chemie* **2017**, *643*, 772.
13. Ding, J. *et al.*, *React. Kinet. Mech. Catal.* **2018**, *125*, 1007.
14. Jafari, M.; Kadivar, M.; Goli, S. A. H. *Int. Food Res. J.* **2013**, *20*, 1997.
15. Vishwanadham, B.; Khan, A. A.; Bhagvanth Rao, M. *J. Am. Oil Chem. Soc.* **1995**, *72*, 1033.
16. Christy, A.; Fernando, N. R. *Adv. Nat. Appl. Sci.* **2016**, *10*, 146.
17. Nezihe, A.; Elif, D.; Oäzlem, Y.; Tunçer, E. A. *Ind. Eng. Chem. Res.*, **2011**, *50*, 398.