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0273-2289/1559–0291 (Online)/07/136–140/583–594/$30.00

Response Surface Methodological Approach for Optimization of Free Fatty Acid Removal in Feedstock

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Abstract

Fatty acid methyl esters, also referred to as biodiesel, have been determined to have a great deal of potential as substitutes for petro-diesel. In order to optimize conversion yield in the biodiesel production process, feedstocks were previously recommended to be anhydrous, with a free fatty acid content of less than 0.5%. In this study, we removed free fatty acid from feedstock through the use of solid catalysts and response surface methodology. In order to optimize free fatty acid removal, response surface methodology was applied to delineate the effects of five-level-four-factors and their reciprocal interactions on free fatty acid removal. A total of 30 individual experiments were conducted, each of which was designed to study reaction temperature, reaction time, catalyst amounts, or methanol amounts. A statistical model was used to estimate that the optimal free fatty acid removal yield would be 100%, under the following optimized reaction conditions: a reaction temperature of 66.96°C, a catalyst amount of 12.66% (w/v), and a reaction time of 37.65 min. Using these optimal factor values under experimental conditions in three independent replicates, an average conversion yield was well achieved within the values predicted by the model.

Index Entries: Biodiesel; free fatty acid; optimization; response surface methodology.

Introduction

Fatty acid methyl esters (FAMEs) derived from a variety of vegetable oils, animal fats, and waste oils have been shown to evidence low viscosities, similar to those associated with petro-diesel. Additionally, many of the salient characteristics of FAMEs, most notably volumetric heating value,

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cetan number, and flash point have also been shown to be comparable with those of petro-diesel *(1–3)*. Several processes have been previously developed for the production of FAMEs through acid-, alkali-, and enzyme-catalyzed transesterification processes *(3–5)*. Transesterification, also called alcoholysis, involves the displacement of alcohol from an ester by another alcohol, in a process comparable to hydrolysis. Transesterification is generally characterized by a number of consecutive, reversible reactions. The reaction step involves the conversion of triglycerides to diglycerides, followed by the conversion of diglycerides to monoglycerides and of monoglycerides to glycerol at each step *(6,7)*. In the process of transesterification, as it is presently conducted, and is the most used, under alkali-catalyst and short-chain alcohol it tends to produce the highest conversion yields with the shortest reaction times. The primary parameters relevant to transesterification include the molar ratio of vegetable oil to alcohol, the catalysts, reaction temperature and time, free fatty acid contents, and water contents in the oils and fats *(5)*. In alkali-catalyzed transesterification, the oils and alcohol must be substantially anhydrous, as water induces saponification with the oils *(5,8)*. Ma et al. *(9)* suggested that the free fatty acid contents of the refined oil should be as low as possible, less than 0.5%. The recommended amount of alkali-catalyst for the transesterification is between 0.1 and 1% (w/w) of oils and fats *(10)*.

Feedstocks used in the production of FAMEs are generally divided into vegetable oils, animal fats, and waste oils. It has been established that high free fatty acid content in oils induces the destruction and decreases the activity of catalysts, and also results in soap conversion *(11)*. As free fatty acid levels increase, this effect becomes increasingly undesirable, owing to the loss of feedstock, as well as the deleterious effects of soap on glycerin separation. The soaps tend to promote the formation of unstable emulsions, which prevent the separation of FAMEs from glycerin during processing *(12)*. A great deal of research has focused on the evaluation of feedstocks regarding the effects of free fatty acid levels. However, in most cases, alkaline catalysts have been utilized in the process, and the free fatty acids were removed from the process stream as soap, and considered to be waste *(5,12,13)*.

Response surface methodology (RSM) utilizes multiple regression and correlation analyses as tools in order to assess the effects of two or more independent factors on the dependent factors. Central composite rotatable design (CCRD) is a RSM, which is used in the optimization processes of biotechnological procedures *(14–17)*. In this study, we removed the free fatty acids from feedstocks through the application of solid catalysts and RSM. In order to optimize free fatty acid removal, we applied RSM to delineate the effects of five-level-four-factors and their reciprocal interactions on the removal of free fatty acids.

Materials and Methods

Chemicals

The crude rapeseed oil was supplied by Onbio Co. Ltd. (Bucheon, Korea), and its characteristics are summarized in Table 1. The oleic acid was supplied by Duksan Pure Chemical Co. Ltd. (Korea). The Lewatit S1467 and Ionac NM60 were obtained from Hankook Baychemical Co. Ltd. (Korea). The characteristics of Ionac NM60 are summarized in Table 2. The Amberlite IR-120 (Duksan Pure Chemical Co. Ltd., Korea), Amberlite IRA-900 (Sigma-Aldrich Co. Ltd.), and Amberlite 200C (Fluka, Switzerland) used in this study were of reagent grade. The anhydrous methanol was obtained from Fisher Scientific. All other chemicals used were of analytical grade, and the solvent used in the study was dried for 1 d before use, with molecular sieves.

Experimental Procedure

In order to select the appropriate solid catalyst, Ionac NM 60, Lewatit S1467, Amberlite IR-120, Amberlite IRA-900, and Amberlite 200C were applied to the removal reaction with refined rapeseed oil combined with 15% oleic acid, for 30 min at 65°C. During the reactions, some of the samples were withdrawn at set intervals, and the acid values of the samples were determined. The results are expressed as the mean values of at least two independent measurements. In order to optimize the CCRD experimental design, a five-level-four-factor CCRD was adopted in this study, requiring 30 experiments, which included 16 factorial points, eight axial points, and six central points to provide information about the interior of the experiment region, allowing evaluation for curvature *(16,17)*. The variables, selected for the study of free fatty acid removal, and their respective levels, were as follows: reaction temperature (30–70°C), catalyst amount (5–20 wt%), reaction time (5–60 min), and methanol amount (0–20 wt%). Table 3 shows the coded and uncoded independent factors (X_i), levels, and experimental design.

All experiments concerning the removal of free fatty acid from oil with a solid catalyst were conducted using a bottle apparatus, with a working volume of 25 mL. The reaction temperature was controlled with a water bath equipped with a PID temperature controller. Mixing was conducted with a magnetic stirrer, spinning at approx 200 rpm. The condenser prevented evaporation of the reactants. During the reactions, some of the samples were withdrawn at set intervals, and the acid values of the samples were determined.

Statistical Analysis

The experimental data (Table 4) were analyzed by means of RSM to fit the following second-order polynomial equation, using Design-Expert 6

Table 1
Composition of Crude Rapeseed Oil

Composition	Content (%)
Triglyceride	94.1
Free fatty acid	4.0
Phospholipid	0.1
Unsaponicable material	1.5
Moisture	0.3

Table 2
Typical Physical and Chemical Properties of Catalyst

Ionic forms	H^+/OH^-
Bead size (mm)	>90; 0.3–1.25
Effective size (mm)	0.47 ± 0.06
Density (g/mL)	1.2
Water retention	55–60
Total capacity (min)	20,000 Ohm-cm; 0.55 eq/L
Stability	Temperature range: 1–49°C; pH range: 0.0–14.0

Table 3
Factors and Their Levels for Central Composite Design

		Coded factor levels				
Variable	Symbol	–2	–1	0	1	2
Reaction temperature (°C)	X_1	30	40	50	60	70
Catalyst amount (wt%)	X_2	5.00	8.75	12.50	16.25	20.00
Reaction time (min)	X_3	5.00	18.75	32.50	46.25	60.00
Methanol amount (wt%)	X_4	0.00	5.00	10.00	15.00	20.00

software (Stat-Ease Inc.). The second-order coefficients were generated through regression with stepwise elimination. The response was initially fitted to the factors through multiple regression. The quality of fit of the model was evaluated through coefficients of determination (R^2) and analysis of variances (ANOVA). The insignificant coefficients were eliminated after the examination of the coefficients, and the model was finally refined. The quadratic response surface model was then fitted to the following equation:

$$Y = \beta_{k0} + \sum_{i=1}^{4} \beta_{ki} x_i + \sum_{i=1}^{4} \beta_{kii} x_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{4} \beta_{kij} x_i x_j \quad (1)$$

Table 4
Central Composite Rotatable Second-Order Design, Experimental and Estimated Data for Five-Level-Four-Factor Response Surface Analysis

Standard	Run	Temperature X_1 (°C)	Catalyst amount (wt%), X_2	Reaction time (min), X_3	Methanol amount (wt%), X_4	Conversion yield (%)	
						Experimental	Estimated
1	2	–1	–1	–1	–1	62.1	65.0
2	21	1	–1	–1	–1	85.3	81.8
3	22	–1	1	–1	–1	87.4	85.3
4	11	1	1	–1	–1	93.7	93.3
5	29	–1	–1	1	–1	90.5	90.8
6	10	1	–1	1	–1	93.7	96.2
7	3	–1	1	1	–1	93.7	97.6
8	6	1	1	1	–1	95.8	94.4
9	27	–1	–1	–1	1	66.3	65.0
10	9	1	–1	–1	1	87.4	81.8
11	4	–1	1	–1	1	87.4	85.3
12	16	1	1	–1	1	93.7	93.3
13	1	–1	–1	1	1	91.6	90.8
14	28	1	–1	1	1	95.8	96.2
15	17	–1	1	1	1	93.7	97.6
16	24	1	1	1	1	95.8	94.4
17	8	–2	0	0	0	89.5	87.4
18	30	2	0	0	0	95.8	100.9
19	14	0	–2	0	0	74.7	76.7
20	25	0	2	0	0	95.8	95.1
21	20	0	0	–2	0	59.0	64.6
22	23	0	0	2	0	95.8	91.4
23	13	0	0	0	–2	93.7	94.1
24	7	0	0	0	2	95.8	94.1
25	12	0	0	0	0	93.7	94.1
26	5	0	0	0	0	93.7	94.1
27	15	0	0	0	0	95.8	94.1
28	26	0	0	0	0	93.7	94.1
29	19	0	0	0	0	93.7	94.1
30	18	0	0	0	0	93.7	94.1

where Y is the response factor (conversion yield), x_i the ith independent factor, β_0 the intercept, β_i the first-order model coefficients, β_{ii} the quadratic coefficients for the factor i, and β_{ij} is the linear model coefficient for the interaction between factors i and j.

Quantitative Analysis

The free fatty acid contents were determined through AOCS Cd 3a-63. Two to ten grams of each sample was dissolved in 100 mL of diethyl ether : EtOH (1:1) solution. After the addition of 2–3 drops of 1% phenolphthalein

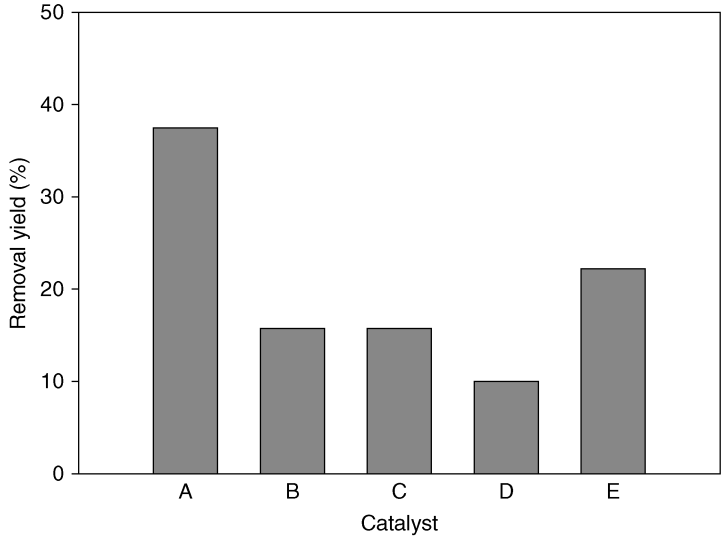

Fig. 1. Effect of kind of catalyst on removal of free fatty acid in prepared rapeseed oil with 15% oleic acid. Reaction temperature was 65°C. A: Ionac NM 60, B: Lewatit S1467, C: Amberlite IR-120, D: Amberlite IRA-900, E: Amberlite 200C.

indicator, the mixed solution was subjected to a titration analysis with alcoholic 0.1 *N* KOH. The free fatty acid contents were calculated as below.

$$\text{Free fatty acid (\%)} = (\text{volume of used KOH solution} - \text{blank}) \times \text{factor} \times 0.1\ N \times 56.11/\text{weight of sample} \times 0.5034.$$

Results and Discussion

In order to optimize the conversion yield of FAMEs production process, it has been previously recommended that the feedstocks be as anhydrous as possible, with a free fatty acid content of less than 0.5% *(5,6,9)*. The primary objective of this study was to optimize free fatty acid removal in crude rapeseed oil using a solid catalyst, coupled with RSM.

First, in order to select the most appropriate solid catalyst for free fatty acid removal, Ionac NM 60, Lewatit S1467, Amberlite IR-120, Amberlite IRA-900, and Amberlite 200C were applied to the removal reaction, with refined rapeseed oil combined with 15% oleic acid for 30 min at 65°C. As is shown in Fig. 1, the removal yield was approx 37.5% with Ionac NM 60. This yield was higher approx 1.7–3.7 times than that of other solid catalysts. For the next experiment, involving the removal of free fatty acids from crude rapeseed oil, Ionac NM 60 was selected as the solid catalyst. Next, in order to estimate the reaction time, waste vegetable oil with an acid value of 2.65 was reacted with the Ionac NM 60 catalyst at 75°C for 1 h. The acid value was decreased to 0.01 after approx 20 min of reaction time (data not shown). In the alkali-catalyzed transesterification process, the free fatty acid amount should be less than 0.5% on the basis of oil weight, in order to obtain a sufficiently high conversion

Table 5
ANOVA for Response Surface-Reduced Quadratic Model

Source	Sum of squares	DF	Mean square	*F*-value	Probability > $F^{a,b}$
Model	2784.92	8	348.11	36.99	<0.0001
X_1	273.62	1	273.62	29.07	<0.0001
X_2	508.81	1	508.81	54.06	<0.0001
X_3	1080.33	1	1080.33	114.79	<0.0001
X_2^2	121.15	1	121.15	12.87	0.0017
X_3^2	463.58	1	463.58	49.26	<0.0001
$X_1 X_2$	75.39	1	75.39	8.01	0.0100
$X_1 X_3$	128.00	1	128.00	13.60	0.0014
$X_2 X_3$	180.06	1	180.06	19.13	0.0003
Residual	197.64	21	9.41	–	–
Lack of fit	193.95	16	12.12	16.42	0.0029
Pure error	3.69	5	0.74	–	–
Correlation total	2982.56	29	–	–	–

[a]Probability > *F*, level of significance.
[b]Values of probability > $F < 0.05$ indicate model terms are significant.

yield *(9)*. Because of its relatively high acid value, the activity of the catalyst was diminished in the transesterification reaction. As is shown in Table 1, the fatty acid content of the crude rapeseed oil used in this experiment was 4%, a value, which is far higher than the proposed value (<0.5%) *(9)*.

In order to construct a proper model for the optimization of free fatty acid removal, the CCRD, which is generally the preferred design for response surface optimization, was selected with five-level-four-factors: reaction temperature, reaction time, catalyst amount, and methanol amount. Table 3 shows the experimental variables settings and the results based on the experimental design. All 30 of the designed experiments were conducted and the results were analyzed through multiregression. The coefficients of the full model were evaluated through regression analysis, and tested for significance. The insignificant coefficients were eliminated in a stepwise manner, on the basis of the *p*-values after the testing of the coefficients. Three linear coefficients (X_1, X_2, X_3), two quadratic coefficients (X_2^2, X_3^2), and three cross-product coefficients (X_1X_2, X_1X_3, X_2X_3) were ultimately determined to be significant (Tables 5 and 6). The final estimative response model equation, after clearing the insignificant variables for the estimation of the effectiveness of free fatty acid removal by stepwise elimination, was as follows.

$$Y = -95.462 + 1.730\,X_1 + 9.905\,X_2 + 3.718\,X_3 - 0.147\,X_2{}^2 - 0.021\,X_3{}^2 - 0.058\,X_1X_2 - 0.021\,X_1X_3 - 0.065\,X_2X_3 \quad (2)$$

Table 6
Regression Coefficients and Significance of Response Surface-Reduced Quadratic Model After a Stepwise Elimination

Factor	Coefficient estimate[a]	DF	Standard error	95% CI low	95% CI high
Intercept	94.15	1	0.886	92.304	95.988
X_1	3.38	1	0.626	2.074	4.679
X_2	4.60	1	0.626	3.302	5.907
X_3	6.71	1	0.626	5.407	8.012
X_2^2	–2.06	1	0.575	–3.260	–0.868
X_3^2	–4.04	1	0.575	–5.233	–2.841
X_1X_2	–2.17	1	0.767	–3.766	–0.576
X_1X_3	–2.83	1	0.767	–4.423	–1.233
X_2X_3	–3.35	1	0.767	–4.950	–1.760

[a]This value of "coefficient estimate" is calculated on the basis of "coded factor level."

where Y is the response factor, conversion yield (%). X_1, X_2, and X_3 are the real values of the independent factors, reaction temperature (°C), catalyst amount (wt%), and reaction time (minutes), respectively. The model coefficients (based on coded factor level) and probability values are fully provided in Table 6. The *p*-values of all of the coefficients were less than 0.05, and the coefficient of determination (R^2) was 0.934, thereby indicating that the model was sufficient to adequately represent the actual relationship among the selected factors. The ANOVA for the response surface-reduced quadratic model is given in Table 5. The coefficients of the response surface model, as are shown by Eq. 1 were evaluated. The *p*-value test showed that all the linear coefficients were all more highly significant than their quadratic and cross-product terms. However, in order to minimize error, all of the coefficients were considered in this design.

Figure 2A shows the effects of reaction temperature, catalyst amount, and their reciprocal interactions on free fatty acid removal at reaction times of 18.75, 32.00, and 135 min. Reaction temperature also appeared to exert a significant degree of influence on removal rates. Increases in the reaction temperature resulted in higher removal yields at any catalyst amount. Removal yields increased in a linear fashion with increasing reaction temperature and catalyst amounts under short reaction time conditions (18.72 min). However, under long reaction time conditions, a saddle-type free fatty acid removal pattern was observed in the experiments in which reaction temperature and catalyst amount were varied.

Figure 2B shows the effects of different catalyst amounts and reaction times on removal yields at constant reaction temperature (50°C). At any of the tested catalyst amounts, from 8.8 to 16.3%, the enhancement of linear removal yields resulted in a low reaction temperature (40°C). As is shown in Figs. 2B (b) and (c), removal yield was maximized at a catalyst amount of 15%

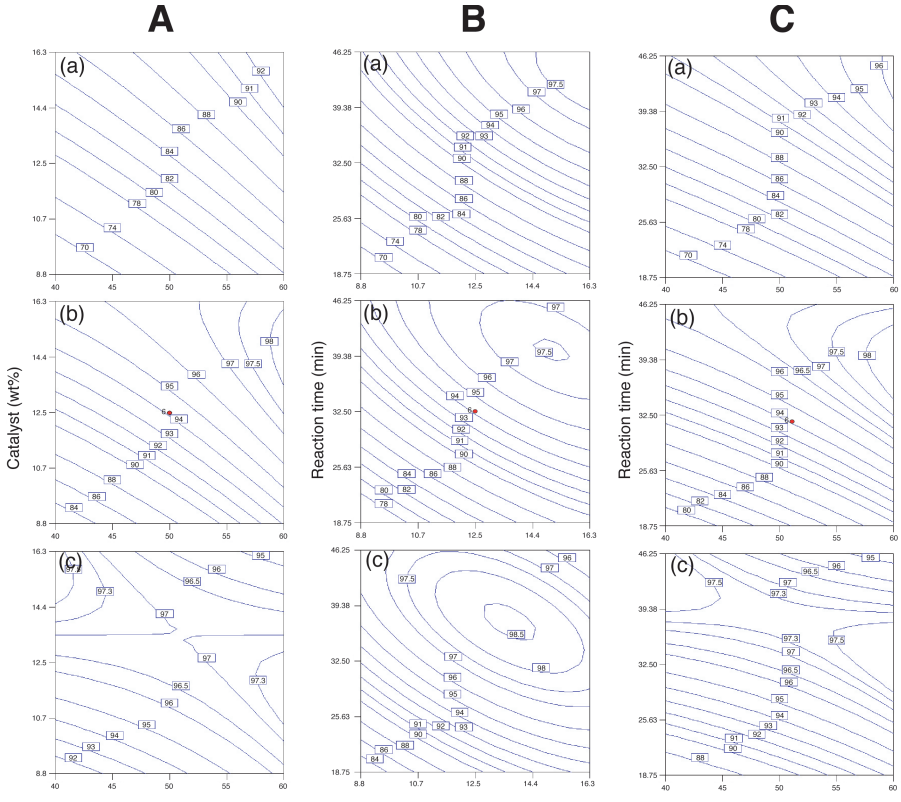

Fig. 2. Contour plots representing the effect of reaction temperature, catalyst amount, reaction time, and their reciprocal interaction on removal yield of free fatty acid in crude rapeseed oil. **(A)** (a) reaction time 18.75 min, (b) 32.00 min, and (c) 46.25 min. **(B)** (a) reaction temperature 40°C, (b) 50°C, and (c) 60°C. **(C)** (a) Catalyst amount 8.75% (w/v), (b) 12.50% (w/v), and (c) 16.25% (w/v).

at 40 min of reaction time at 50°C; however, these values peaked at a catalyst amount of 13% and 37 min. Maximal yield was accomplished with a high catalyst amount and a long reaction time, at a high reaction temperature. At any of the designed reaction temperatures, increases in the catalyst amount resulted in a linear enhancement of removal yields to optimum conditions.

Figure 2C shows the effects of reaction temperature, reaction time, and the reciprocal interaction of these factors with free fatty acid removal rates at constant catalyst amounts of 8.75, 12.50, and 16.25% (w/v). As is shown in Figs. 2C (a) and (c), reaction temperature also exerted a significant degree of influence on removal rates. Increases in reaction temperature resulted in high removal yields at any of the tested constant catalyst amounts. Removal yields were shown to increase in a linear fashion with reaction temperature and reaction times at low catalyst amounts (8.75%). However, at high catalyst amounts, a saddle pattern of free fatty acid removal was observed in the experiments in which reaction temperature and time were varied.

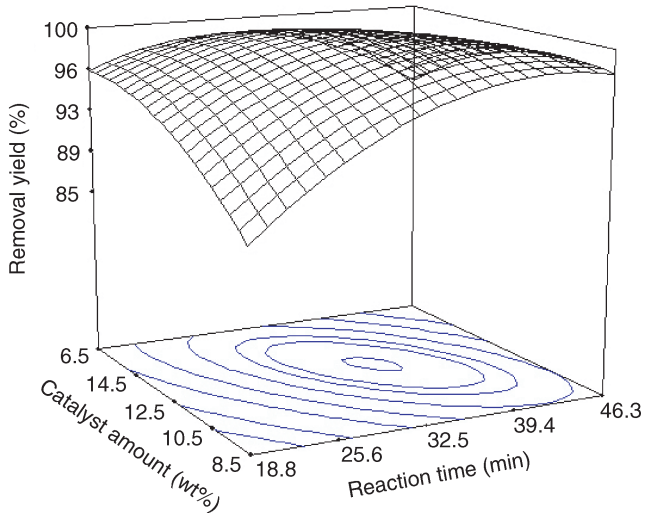

Fig. 3. Response surface plot representing the effect of reaction time and catalyst amount of the optimal removal of free fatty acid in crude rapeseed oil at the stationary point (reaction temperature 66.96°C).

Figure 3 contains the response surface plot showing the effects of reaction time and catalyst amount on free fatty acid removal rates in crude rapeseed oil. The optimal conditions for free fatty acid removal estimated by the model equation were as follows: $X_1 = 66.96$°C, $X_2 = 12.66\%$, and $X_3 = 37.65$ min. The theoretical removal yield estimated under the aforementioned conditions was $Y = 100\%$. In order to confirm this model-based estimation, the predicted optimal conditions were applied to three independent replicates for free fatty acid removal. The average removal yield proved to be well within the values estimated through the model equation. This shows that RSM coupled with the appropriate experimental design can be applied effectively to the optimization of factors in a reaction *(17)*. This study focused specifically on the application of RSM for the optimization of conditions for free fatty acid removal using a solid catalyst in feedstock. Our results may provide useful information regarding the development of more economical and efficient solid catalyst system for biodiesel production processes.

Acknowledgments

The authors would like to thank the Korea Energy Management Corporation for their financial support of this study.

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