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Research Article

Saponification of *Jatropha curcas* Seed Oil: Optimization by D-Optimal Design

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In this study, the effects of ethanolic KOH concentration, reaction temperature, and reaction time to free fatty acid (FFA) percentage were investigated. D-optimal design was employed to study significance of these factors and optimum condition for the technique predicted and evaluated. The optimum conditions for maximum FFA% were achieved when 1.75 M ethanolic KOH concentration was used as the catalyst, reaction temperature of 65°C, and reaction time of 2.0 h. This study showed that ethanolic KOH concentration was significant variable for saponification of *J. curcas* seed oil. In an 18-point experimental design, percentage of FFA for saponification of *J. curcas* seed oil can be raised from 1.89% to 102.2%.

1. Introduction

Saponification of oils is the applied term to the operation in which ethanolic KOH reacts with oil to form glycerol and fatty acids. Production of fatty acid and glycerol from oils is important especially in oleochemical industries. Glycerol and fatty acids are widely used as raw materials in food, cosmetics, pharmaceutical industries [1, 2], soap production, synthetic detergents, greases, cosmetics, and several other products [3]. The soap production starting from triglycerides and alkalis is accomplished for more than 2000 years by [4].

These reactions produce the fatty acids that are the starting point for most oleochemicals production. As the primary feedstocks are oils and fats, glycerol is produced as a valuable byproduct. Reaction routes and conditions with efficient glycerol recovery are required to maximize the economics of large-scale production [5]. Lipid saponification is usually carried out in the laboratory by refluxing oils and fats with different catalysts [6]. The reaction can be catalyzed by acid, base, or lipase, but it also occurs as an uncatalyzed reaction between fats and water dissolved in the fat phase at suitable temperatures and pressures [7].

Researchers have used several methods to saponify oils such as enzymatic saponification using lipases from *Aspergillus niger*, *Rhizopus javanicus*, and *Penicillium solitum* [8], *C. rugosa* [1], and subcritical water [3]. Historically, soaps were produced by alkaline saponification of oils and fats, and this process is still referred to as saponification. Soaps are now produced by neutralization of fatty acids produced by fat splitting, but alkaline saponification may still be preferred for heat-sensitive fatty acids [9]. Nowadays, researchers have used potassium hydroxide-catalyzed hydrolysis of esters which is sometimes known as saponification because of its relationship with soap making. There are two big advantages of doing this. The reactions are one way rather than reversible, and the products are easier to separate as shown in [3].

This study is executed for the factors that affect the process for saponification of *J. curcas* seed oil. D-optimal design was used to evaluate the effect of three factors, such as ethanolic KOH concentration, reaction temperature, and reaction time which were studied for the optimum saponification.

2. Methodology

2.1. Experimental Procedure. FAs were obtained by the saponification of *J. curcas* seed oil, as carried out by [10]. Table 1 shows the different concentration of ethanolic KOH, different reaction temperature, and different reaction time

Table 1: Independent variables and their levels for D-optimal design of the saponification reaction.

Independent variables		Variable levels		
		−1	0	+1
KOH (M)	X_1	1.00	1.50	2.00
Temperature (°C)	X_2	50	60	70
Time (h)	X_3	1.5	2.0	2.5

using D-optimal design. Factors such as ethanolic KOH concentration (M, X_1), reaction temperature (°C, X_2), and reaction time (h, X_3) were performed under the same experimental conditions in order to verify them using the KOH saponification of *J. curcas* seed oil. In a typical experiment, *J. curcas* seed oil 50 g was mixed in the reactor with 300 mL of saponifying solution comprising of ethanolic KOH concentration (1.00–2.00 M) and ethanol (300 mL: 90% v/v). The saponification was carried out in a 500 mL temperature-controlled reactor at different temperatures 50–70°C and for different times 1.5–2.5 h. After saponification, 200 mL water was added. Unsaponifiables were separated by extraction with hexane 100 mL. The aqueous alcohol phase, containing the soaps, was acidified to pH 1 with HCl 6N, and the free fatty acids (FFAs) were recovered by extraction with hexane. The extract was washed with distilled water to neutral pH. The resulting lower layer was removed using a separating funnel and discarded. The FFA-containing upper layer was dried with anhydrous magnesium sulphate, and solvent was evaporated in a vacuum rotary evaporator at 35°C. The FFA% and the FAs composition from saponified *J. curcas* seed oil were determined using GC-FID according to [11].

2.2. Experimental Design and Statistical Analysis. A three-factor D-optimal design was employed to study the responses of the FFA% (Y in %, by wt, see (1)). An initial screening step was carried out to select the major response factors and their values. The independent variables were X_1, X_2, and X_3 representing the concentration of ethanolic KOH (M), reaction temperature (°C), and reaction time (h), respectively. The settings for the independent variables were as follows (low and high values): KOH concentration of 1.0 and 2.0, reaction temperature of 50 and 70, and reaction time of 1.5 and 2.5. Each variable to be optimized was coded at three levels: −1, 0, and +1. A quadratic polynomial regression model was assumed for predicting individual Y variables. The model proposed for each response of Y was

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \sum \beta_{ij} x_i x_j, \quad (1)$$

where β_0, β_i, β_{ii}, and β_{ij} are constant, linear, square, and interaction regression coefficient terms, respectively, and x_i and x_j are independent variables. The Minitab software version 14 (Minitab Inc., USA) was used for multiple regression analysis, analysis of variance (ANOVA), and analysis of ridge maximum of data in the response surface regression (RSREG) procedure [12].

3. Results and Discussion

D-optimal design was employed to study the percentage of FFA by ethanolic KOH saponification of *J. curcas* seed oil. Experimental results of the percentage of FFA for ethanolic KOH reactions with *J. curcas* seed oil are given in Table 2.

The results show the saponification performances of the ethanolic KOH effects on the saponification reaction when submitted to different experimental conditions. Table 2 illustrates the variation of the percentage of FFA when, simultaneously, the concentration of the ethanolic KOH is analyzed. For 1.00 M of ethanolic KOH, practically no effect on the percentage of FFA was observed. On the other hand, increase in the concentration of ethanolic KOH (1.00, 1.50, 1.75, and 2.00 M, resp.) showed increas in the percentage of FFA, which has the highest value of FFA% at 1.75 M ethanolic KOH (102.2%) and has been chosen for the optimum conditions as can be seen in Table 2. A different observation was reported by other researchers for saponification of various vegetable using *C. rugosa* lipase [13–15]. Increase in enzyme concentration did not give any significant changes in the reaction rate [15].

Table 2 displays a general view of the behavior of the saponification yield as a function of the different temperatures (50, 60, 65, and 70°C). However, the results show with increase the reaction temperature increases the saponification of *J. curcas* seed oil in positive way or vice versa, which means that the maximum of the saponification (102.2%) at 65°C has been chosen for the optimum conditions as shown in Table 2. This theory has been reported by [1] by using enzyme *C. rugosa* lipase. Increasing of the reaction temperature has affected the production of fatty acids which clearly showed an increase in conversion.

Table 2 indicates the percentage of FFA using different times (1.5, 2.0, and 2.5 h) with different variables such as concentration of ethanolic KOH and reaction temperatures. As shown in Table 2, percentage of FFA increases with increasing the reaction time. Furthermore, 2.0 h was chosen to obtain highest percentage of FFA (102.2%). The quadratic regression coefficient obtained by employing a least-squares method technique to predict quadratic polynomial models for the percentage of FFA (Y) is given in Table 3.

Examination of these coefficients with a t-test shows that for the percentage of FFA in the concentrate (Y) the linear, square, and interaction terms of concentration of ethanolic KOH (X_1) were highly significant ($P < 0.01$), and the linear terms of the reaction temperature (X_2) were also highly significant ($P < 0.01$), while the reaction time (X_3) for the percentage of FFA (Y) in the concentrate was significant at $P < 0.05$. The coefficients of independent variables (concentration of KOH: X_1, temperature: X_2, and time: X_3) determined for the quadratic polynomial models (Table 3) for the percentage of FFA (Y) are given below:

$$\begin{aligned} Y = {} & +96.65 + 17.28X_1 + 4.33X_2 + 1.91X_3 \\ & - 15.14{X_1}^2 + 0.37{X_2}^2 + 0.63{X_3}^2 - 3.48X_1X_2 \\ & - 1.40X_1X_3 + 0.11X_2X_3. \end{aligned} \quad (2)$$

Table 2: D-optimal design optimization of *J. curcas* seed oil saponification and response for FFA%.

Run	Coded independent variable levels			Response
no.	Ethanolic KOH (M, X_1)	Temperature (°C, X_2)	Time (h, X_3)	FFA (%, Y)
1	2.00	50	1.5	97.1
2	2.00	70	2.5	102.4
3	1.00	50	1.5	53.9
4	1.00	60	2.0	64.6
5	2.00	50	2.5	97.5
6	1.75	65	2.0	102.2
7	2.00	50	2.5	99.1
8	1.00	50	2.5	60.8
9	1.00	70	2.5	77.1
10	1.50	60	2.5	97.4
11	1.00	50	2.5	67.9
12	2.00	60	1.5	100.3
13	1.00	50	1.5	55.1
14	1.00	70	1.5	70.0
15	1.50	50	2.0	96.72
16	2.00	70	1.5	100.4
17	1.00	70	2.5	72.4
18	1.50	70	1.5	99.2

Table 3: Regression coefficients of the predicted quadratic polynomial model for response variables Y (FFA%).

Variables	Coefficients (β) % FFA (Y)	t	P	Notability
Intercept linear	96.65	144.21	0.0001	***
X_1	17.28	889.81	0.0001	***
X_2	4.33	57.02	0.0001	***
X_3	1.91	9.52	0.0150	**
Square				
X_{11}	−15.14	130.05	0.0001	***
X_{22}	0.37	0.085	0.7777	
X_{33}	0.63	0.33	0.5838	
Interaction				
X_{12}	−3.48	30.63	0.0006	***
X_{13}	−1.40	4.02	0.0800	
X_{23}	0.11	0.023	0.8825	
R^2	0.99			

**$P < 0.05$; ***$P < 0.01$. T: F test value
See Table 2 for a description of the abbreviations.

Table 4: Analysis of variance (ANOVA) of the response Y for FFA%.

Source	Df[a]	Sum of squares	Mean square	F-value[b]	Prob > F	
Model	9	5592.97	621.44	84.70	<0.0001	Significant
Residual	8	58.70	7.34			
Lack-of-fit	4	20.45	5.11	0.53	0.7205	Not significant
Pure error	4	38.25	9.56			

[a]Df: degree freedom; [b]F-value: distribution.

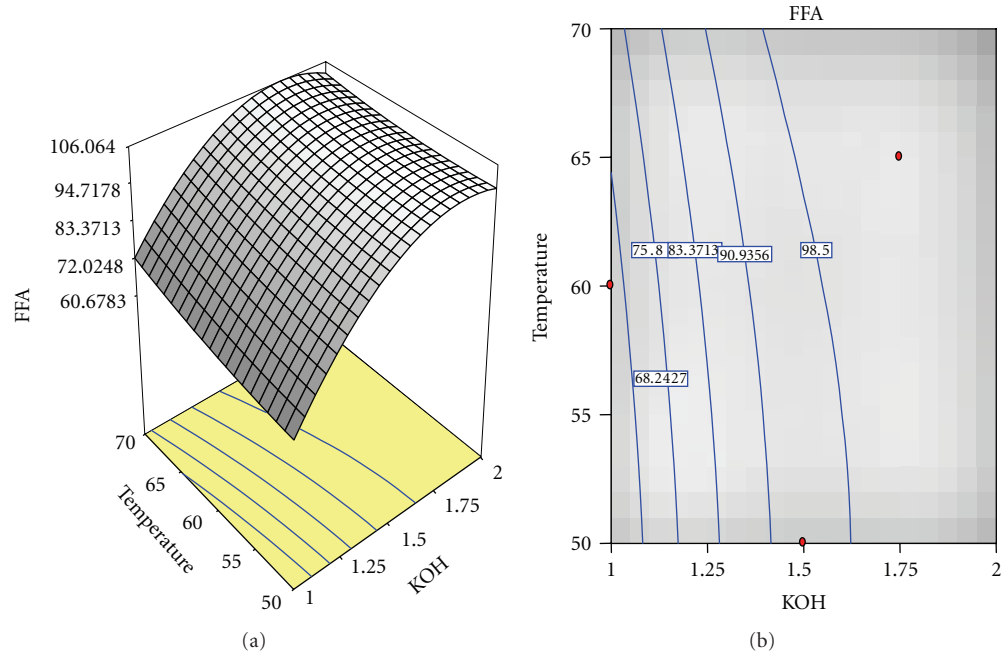

Figure 1: Response surface (a) and contour plots (b) for the effect of the ethanolic KOH (X_1, w) and reaction temperature (X_2, °C) on the FFA%.

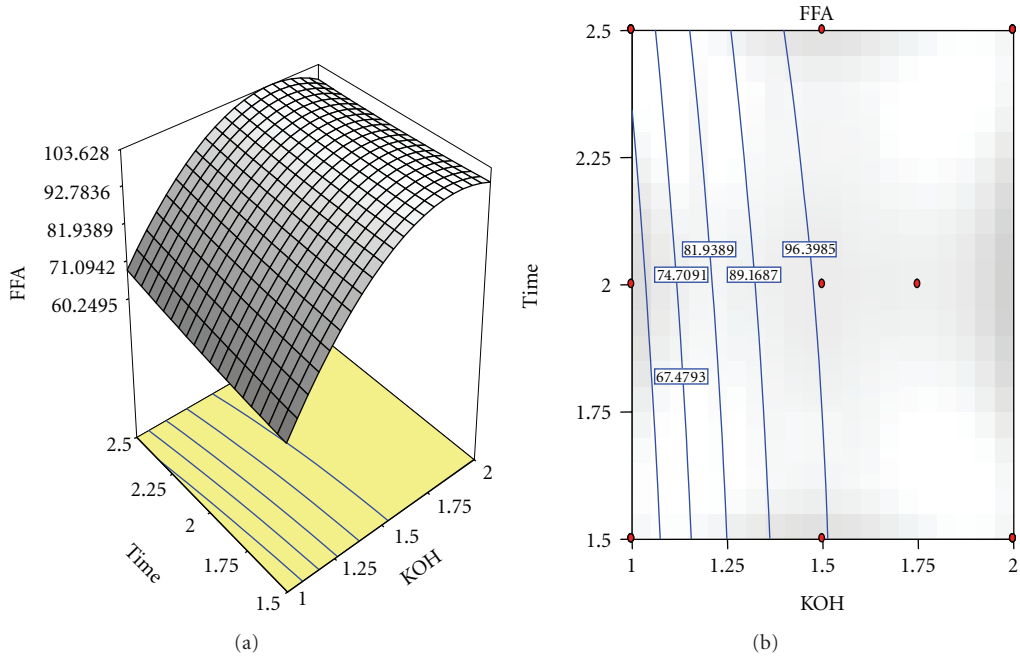

Figure 2: Response surface (a) and contour plots (b) for the effect of the ethanolic KOH (X_1, w) and reaction time (X_3, h) on the FFA%.

ANOVAs for the fitted models are summarized in Table 4. Examinations of the model with an F-test and t-test indicate a nonsignificant lack of fit at $P > 0.05$ relative to pure error (9.56%). The regression coefficient (R^2) for data on the percentage of FFA was 0.99 (Table 3).

Equation (2) showed that the percentage of FFA has a complex relationship with independent variables that encompass both first- and second-order polynomials. Response surface methodology (RSM) is one of the best ways of evaluating the relationships between responses, variables, and interactions that exist. Significant interaction variables in the fitted models (Table 3) were chosen as the axes (concentration of KOH: X_1, temperature: X_2, and time: X_3) for the response surface plots. The relationships between

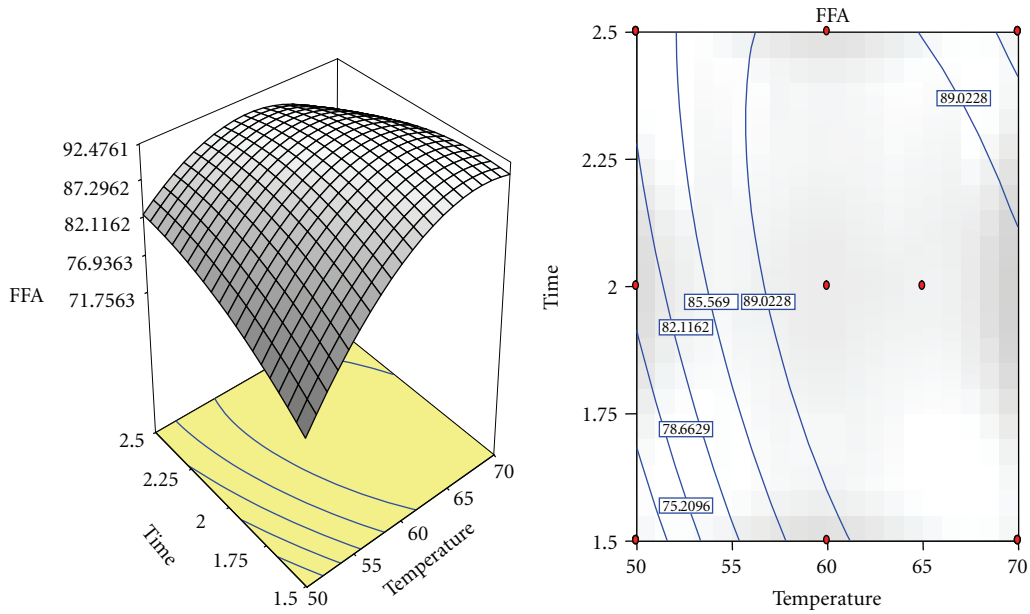

Figure 3: Response surface (a) and contour plots (b) for the effect of the reaction temperature (X_2, °C) and reaction time (X_3, h) on the FFA%.

Table 5: D-optimal design arrangement for the concentration effect of ethanolic alkaline solution KOH, temperature (°C) and time (h) to the FAs composition before and after the saponification.

Fatty acids	FA% before saponification[a]	FA% saponification 1.00 M[b]	FA% saponification 1.50 M[c]	FA% saponification 1.75 M[d]
Palmitic	13.19	13.55	13.06	13.07
Palmitoleic	0.40	0.64	0.56	0.55
Stearic	6.36	4.52	6.78	6.80
Oleic	43.32	43.94	43.97	43.03
Linoleic	36.70	37.32	36.46	36.51

[a] *J. curcas* seed oil, [b, c, d] saponification at 70° C.

independent and dependent variables are shown in the three-dimensional representation as response surfaces. The response surfaces for the percentage of FFA (Y) in the concentrates were given in Figures 1, 2, and 3.

The contour plot (Figures 1(b), 2(b), and 3(b)) shows the combination of levels of the concentration of KOH and saponification temperature that can afford the same level of the percentage of FFA. Canonical analysis was performed on the predicted quadratic polynomial models to examine the overall shape of the response surface curves and was used to characterize the nature of the stationary points. Canonical analysis is a mathematical approach used to locate the stationary point of the response surface and to determine whether it represents a maximum, minimum, or saddle point [16].

The model of saponification FFA was developed on the basis of the analysis of RSM. The concentration of KOH was the most important parameter for the percentage of FFA, and the observed value was reasonably close to the predicted value as shown in Figure 4. The process may help produce high percentage of FFA from an economic point of view, as well as being a promising measure for further utilization of agriculture products.

D-optimal design was employed to study the composition of FFA by ethanolic KOH saponification of *J. curcas* seed oil through FAMEs analysis before and after the saponification. The analyses made by GC-FID had a positive identification of acids fatty. Experimental results of the percentage of the composition of FFA for ethanolic KOH reactions with *J. curcas* seed oil are given in Table 5. The comparative data indicate that no significant difference under the optimum conditions $P < 0.05$.

Table 5 shows a comparison the composition of fatty acids before the saponification (a) and after saponification at different ethanolic KOH concentration (b and c, resp.) as determined directly by GC-FID, through FAMEs analysis. Intermediate products formed in the saponification, as well as the methyl esters by FAMEs [17]. The comparative data indicate that the saponification does not cause the decomposition of the fatty acids.

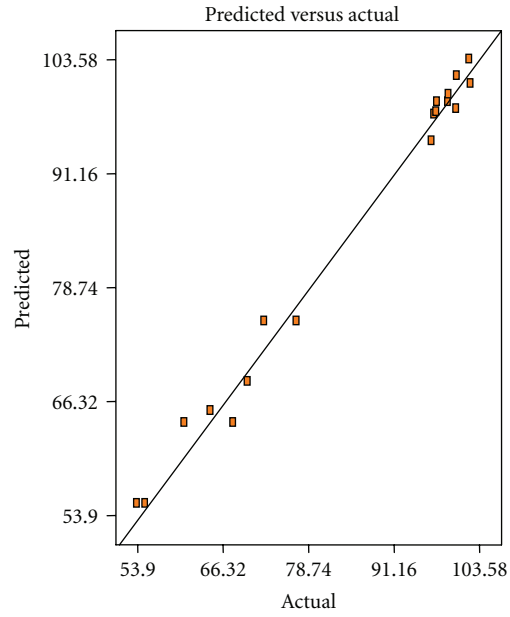

Figure 4: Predicated versus actual plot of Y.

4. Conclusion

D-optimal design provided a powerful tool to optimize the saponification conditions that permit an important improvement in the percentage of saponification. The results indicate that the optimization using a response surface methodology based on D-optimal design was useful software in improving the optimization of FFA%.

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References

[1] N. A. Serri, A. H. Kamarudin, and S. N. Abdul Rahaman, "Preliminary studies for production of fatty acids from hydrolysis of cooking palm oil using C. rugosa lipase," *Journal of Physical Science*, vol. 19, pp. 79–88, 2008.

[2] H. Hermansyah, M. Kubo, N. Shibasaki-Kitakawa, and T. Yonemoto, "Mathematical model for stepwise hydrolysis of triolein using Candida rugosa lipase in biphasic oil-water system," *Biochemical Engineering Journal*, vol. 31, no. 2, pp. 125–132, 2006.

[3] J. S. S. Pinto and F. M. Lanças, "Hydrolysis of corn oil using subcritical water," *Journal of the Brazilian Chemical Society*, vol. 17, no. 1, pp. 85–89, 2006.

[4] O. J. Ackelsberg, "Fat splitting," *Journal of the American Oil Chemists Society*, vol. 35, pp. 635–640, 1958.

[5] C. Scrimgeour, "Chemistry of fatty acid," in *Bailey fs Industrial Oil and Fat Products*, F. Shahidi, Ed., vol. 5, pp. 1–43, John Wiley & Sons, Hoboken, NJ, USA, 6th edition, 2005.

[6] F. D. Gunstone, *The Chemistry of Oils and Fats: Sources, Composition, Properties, and Uses*, Blackwell, 2004.

[7] A. Rukmini and S. Raharjo, "Pattern of peroxide value changes in virgin coconut oil (VCO) due to photo-oxidation sensitized by chlorophyll," *Journal of the American Oil Chemists' Society*, vol. 87, no. 12, pp. 1407–1412, 2010.

[8] P. O. Carvalho, P. R. B. Campos, M. D'Addio Noffs, P. B. L. Fregolente, and L. V. Fregolente, "Enzymatic hydrolysis of salmon oil by native lipases: optimization of process parameters," *Journal of the Brazilian Chemical Society*, vol. 20, no. 1, pp. 117–124, 2009.

[9] W. W. Christie, *Lipid Analysis*, The Oily Press, Bridgwater, UK, 3rd edition, 2002.

[10] H. B. Hashim and J. Salimon, "Kajian pengoptimuman tindak balas hidrolisis minyak kacang soya," *The Malaysian Journal of Analytical Sciences*, vol. 12, pp. 205–209, 2008.

[11] AOCS, *Official Methods of Analysis*, Association of Official Analytical Chemist, Arlington, Tex, USA, 16th edition, 1997.

[12] M. Wu, H. Ding, S. Wang, and S. Xu, "Optimizing conditions for the purification of linoleic acid from sunflower oil by urea complex fractionation," *Journal of the American Oil Chemists' Society*, vol. 85, no. 7, pp. 677–684, 2008.

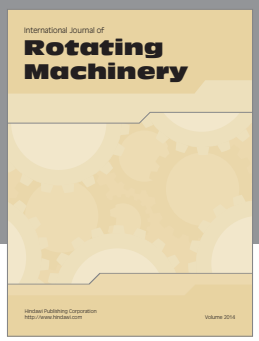
[13] I. M. Noor, M. Hasan, and K. B. Ramachandran, "Effect of operating variables on the hydrolysis rate of palm oil by lipase," *Process Biochemistry*, vol. 39, no. 1, pp. 13–20, 2003.

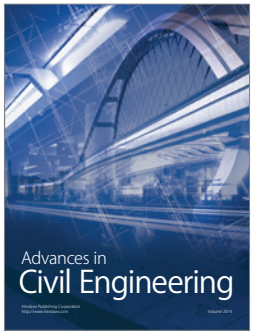
[14] S. Fadiloğlu and Z. Söylemez, "Olive oil hydrolysis by celite-immobilized Candida rugosa lipase," *Journal of Agricultural and Food Chemistry*, vol. 46, no. 9, pp. 3411–3414, 1998.

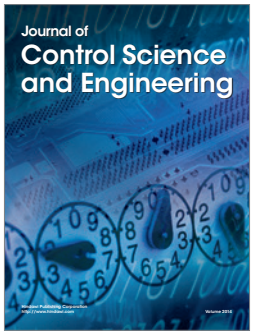
[15] D. Rooney and L. R. Weatherley, "The effect of reaction conditions upon lipase catalysed hydrolysis of high oleate sunflower oil in a stirred liquid-liquid reactor," *Process Biochemistry*, vol. 36, no. 10, pp. 947–953, 2001.

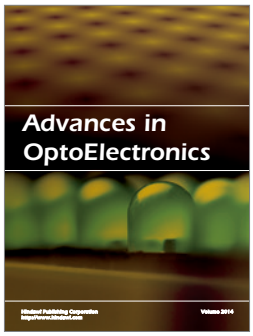
[16] R. L. Mason, R. F. Gunst, and J. L. Hess, *Statistical Design and Analysis of Experiments with Applications to Engineering and Science*, John Wiley & Sons, New York, NY, USA, 1989.

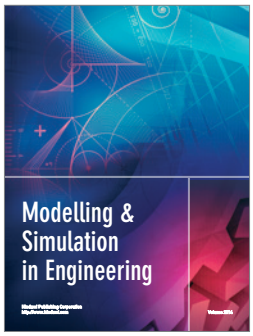
[17] J. Salimon, B. M. Abdullah, and N. Salih, "Hydrolysis optimization and characterization study of preparing fatty acids from Jatropha curcas seed oil," *Chemistry Central Journal*, vol. 5, articel 67, 2011.

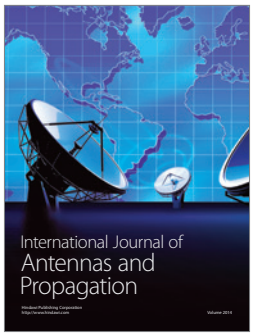


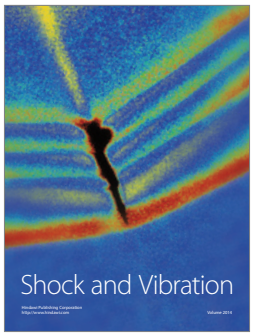


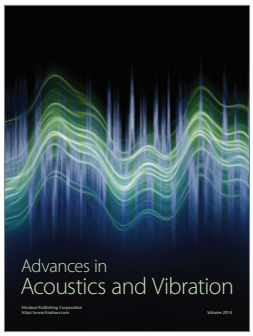












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