Tối ưu hóa dựa trên thiết kế tổng hợp trung tâm (CCD) cho quá trình chuyển hóa axit béo tự do trong dầu chiết xuất từ bã cà phê thành diesel sinh học

Phan Thị Thanh Phương[1], Võ Văn Tiến[1], Nguyễn Việt Quang[1], Lê Thị Thanh Ngân[1], Đặng Nguyên Thoại[1,2,*]

[1]Khoa Khoa học Tự nhiên, Trường Đại học Quy Nhơn, Việt Nam
[2]Trung tâm Hỗ trợ sinh viên và Quan hệ doanh nghiệp, Trường Đại học Quy Nhơn, Việt Nam

Ngày nhận bài: 26/03/2021; Ngày sửa bài: 14/04/2021;
Ngày nhận đăng: 22/04/2021; Ngày xuất bản: 28/06/2021

TÓM TẮT

Hiện nay, dầu chiết xuất từ bã cà phê (WCGO) đã chứng minh là nguồn nguyên liệu phù hợp để sản xuất diesel sinh học. Tuy nhiên, vì hàm lượng axit béo tự do (FFA) cao trong dầu được trích ly từ bã cà phê nên cần có quá trình tiền xử lý. Trong nghiên cứu này, phản ứng este hóa giữa FFA trong dầu được chiết xuất từ bã cà phê với methanol được thực hiện trong thiết bị phản ứng khuấy trộn, làm việc gián đoạn. Phương pháp bề mặt đáp ứng (RSM) được áp dụng để thiết lập các thí nghiệm, phân tích, đánh giá và tối ưu hóa kết quả thực nghiệm. Các điều kiện thực nghiệm bao gồm: tỷ lệ mol giữa methanol/WCGO (5 – 10 mol/mol), hàm lượng xúc tác H_2SO_4/WCGO (1 – 10% kl), nhiệt độ phản ứng (50 – 70 ^oC) và thời gian phản ứng (60 – 120 phút). Ảnh hưởng của các điều kiện thực nghiệm đã được đánh giá và kiểm tra nhờ phương pháp RSM. Mô hình hồi quy cho quá trình chuyển hóa FFA trong WCGO thành biodiesel đã được xác thực bởi hệ số tương quan cao (R^2 = 0,923). Độ chuyển hóa FFA đạt được 90% (ứng với hàm lượng FFA cuối cùng đạt 0,7% kl) với tỷ lệ mol MeOH/WCGO là 8,18 mol/mol, hàm lượng xúc tác H_2SO_4/WCGO là 8,74% kl trong thời gian phản ứng 90 phút tại nhiệt độ 60 ^oC. Cuối cùng, một vài chỉ tiêu quan trọng của sản phẩm ester hóa được được kiểm tra phù hợp cho các giai đoạn tiếp theo của quá trình sản xuất diesel sinh học.

Từ khóa: *Diesel sinh học, bã cà phê, WCGO, este hóa, RSM.*

*Tác giả liên hệ chính.
Email: dangnguyenthoai@qnu.edu.vn

https://doi.org/10.52111/qnjs.2021.15309

QUY NHON UNIVERSITY
JOURNAL OF SCIENCE

Central composite design-based optimization for conversion of free fatty acids in oil extracted from coffee grounds into biodiesel

Phan Thi Thanh Phuong[1], Vo Van Tien[1], Nguyen Viet Quang[1], Le Thi Thanh Ngan[1], Dang Nguyen Thoai[1,2,*]

[1]Faculty of Natural Sciences, Quy Nhon University, Vietnam
[2]Center for Student Support and Enterprise Relations, Quy Nhon University, Vietnam

Received: 26/03/2021; Revised: 14/04/2021;
Accepted: 22/04/2021; Published: 28/06/2021

ABSTRACT

Extracted oil from waste coffee grounds (WCGO) has proven to be a suitable sources to produce biodiesel. However, they needs to be pretreated because of high free fatty acid (FFA) content in WCGO. In this study, the esterification reaction between FFA in extracted oil from coffee grounds with methanol was performed in a batch reactor. Response surface methodology (RSM) was applied to establish experiment, synthesize, evaluvate, and optimize the experiment results. The factors included: MeOH/WCGO molar ratio (5 – 10 mol/mol), H_2SO_4/WCGO catalyst content (1 – 10 wt.%), temperature (50 – 70 ^oC) and reaction time (60 – 120 min). The effects of these factors were evaluated and tested as per RSM. The regression model of conversion of FFA in WCGO to biodiesel was established with a high correlation coefficient (R^2 = 0.923). The FFA conversion of 90% (final FFA content of 0.70 wt%) was achieved with the MeOH/WCGO molar ratio of 8.18 mol/mol, H_2SO_4/WCGO catalyst content of 8.74 wt.% for 90 min at 60 ^oC. Finally, some important properties of the esterified oil were checked for the suitability for the next stage of biodiesel production.

Keywords: *Biodiesel, Waste coffee ground, WCGO, esterification, RSM.*

1. INTRODUCTION

In general, biodiesel is defined as fatty acid alkyl esters produced from alternative resources via esterification, transesterification or two-step reactions. Its properties are acceptable to be used directly or mixed with petroleum diesel.[1] At the present, the basic resources to produce biodiesel is cooking oils thanks to its low FFA content. Nevertheless, depending on edible vegetable oils is a major drawback to commercial target because of high price and food security.[2] Therefore, many non-edible oils including waste cooking oil, Jatropha oil and waste coffee ground oils (WCGO) have been more and more attractive as renewable resources for biodiesel production with low cost.[1,2]

Vietnam is a country in the top two of the leading coffee producing countries in the world, only after Brazil. In 2019, approximately 2.6 million 60 kg bags of coffee was consumed in Vietnam.[3] By considering this huge amount, the re-use process of WCGO should be made. The WCGOs contains 11 – 20 wt.% of oil hang on its kind.[4,5] WCGO is convinced to become a

**Corresponding author.*
Email: dangnguyenthoai@qnu.edu.vn

https://doi.org/10.52111/qnjs.2021.15309

novel feedstock to create biodiesel. Nonetheless, inedible oils accommodate a high FFA (> 2 wt.%) to be easy to react with the alkaline catalysts to form soap via the saponification reaction. This process take to losing of catalyst and ester and grow the manufacture cost.[1] Therefore, WCGO needs to be treated by esterification reaction to remove FFA as much as possible before transesterification reaction to make biodiesel.

In this work, the esterification of WCGO in the existence of H_2SO_4 as a homogeneous acid catalyst was performed to lessen the FFA content. The aims of this task were: (a) investigating the acid-catalyzed esterification reaction; (b) evaluating the influence of MeOH/WCGO molar ratio, H_2SO_4/WCGO catalyst content, temperature and reaction time on the FFA conversion in WCGO; (c) employing response surface methodology (RSM) to design, analyze, and optimize the experimental conditions; and (d) determining some properties of the esterified oil.

2. MATERIALS AND METHODS

2.1. Materials

Waste coffee grounds (WCGs) were collected from coffee shops in Quy Nhon City, Vietnam. Methanol (MeOH, purity > 99 wt.%) and sulfuric acid (H_2SO_4, purity > 98 wt.%) were purchased from Xilong Scientific Co., Ltd., China. Etanol (EtOH, purity > 99 wt.%) was obtained from Cemaco Vietnam Co., Ltd. – Ho Chi Minh city Branch, Vietnam.

2.2. Extraction of WCGO

First, the WCGs were dried in sunlight for 24 hours to remove its wetness. Second, the dried WCGs were extracted by using ethanol. This mixture was mixed in 15 minutes and then it was disparated from the WCGs by filter.[4] Next, the WCGO was disparated from the solvent by utilizing a vacumn rotary evaporation. The WCGO was kept in the stove in 5 hours at 105 ^oC to separate any ethanol remaining in the extracted WCGO.

2.3. Esterification procedure

The esterification process was conducted in a 0.5-liter three-necked round-bottom flask attached to a thermometer, with magnetic stirring at stirring speed of 600 rpm, reflux by water at 20 ^oC to liquefy the MeOH vapour. The parameters for experiment were chosen and shown as in Table 1. First, the WCGO was preheated up to the temperature extended to the called value. Next, the mix of MeOH and H_2SO_4 (98 wt.%) were added into flask. After finished reaction, the product was poured into the separating tube and settled in 90 min to discrete into two phases (oil phase and aqueous phase). Then, the aqueous phase was taken out of the oil phase, the oil phase was washed with hot water to unfasten the catalyst and the alcohol out of oil phase. This procedure was conducted at 70 ^oC, three times without swaying and three times with swaying. The washed oil phase was dried completely by the reheating at 110 ^oC in 120 minutes.

All experiments were done three times to approximate mistake. Experiments parameters were planned with different conditions including MeOH/WCGO molar ratio (5-10 mol/mol), catalyst content (1-10 wt% H_2SO_4/WCGO), reaction temperature (50-70 ^oC) and reaction time (60-120 minutes).

Table 1. Experimental parameters used in esterification of WCGO

Variables			Limit and coded level				
Variables	Symbol	Unit	-α	-1	0	+1	+α
MeOH/WCGO molar ratio	X_1	mol/mol	5	6.25	7.5	8.75	10
H_2SO_4/WCGO catalyst content	X_2	wt.%	1	3.25	5.5	7.75	10
Reaction temperature	X_3	^oC	50	55	60	65	70
Reaction time	X_4	min	60	75	90	105	120

https://doi.org/10.52111/qnjs.2021.15309

2.4. FFA analysis and FFA conversion

The initial FFA content of the WCGO and the final product were determined based on ASTM D664. First, the sample was accurately weighted about 1 – 10 g into a conical vessel. Then, 50 mL of ethanol was attached and vigorous swung to diffuse this sample. Phenolphtalein was attached about 3 – 5 drops as an indicator. The mix was titrated with 0.1N NaOH up to emerging a continuing pink. The FFA content and FFA conversion were caculated according to the following equations:

$$\%FFA = \frac{(V \times C \times 267.5)\times 100}{1000 \times m} \quad (1)$$

$$X = \frac{\%\mathrm{FFA}_o - \%\mathrm{FFA}}{\%\mathrm{FFA}_o} * 100\% \quad (2)$$

Herein, V and C are volume (mL) and concentration (mol/L) of NaOH, m is the sample weight (g) and 267.5 is the average molecular weight of WCGO's fatty acid (g/mol).[6]

2.5. Experiment designs

Response surface methodology (RSM) is one of modern statistical methods used to determine response behavior.[7] The central composite design (CCD) was applied to discover the best conditions for the wanted FFA conversion. The CCD combines five levels (coded –α, –1, 0, +1,+α, as in Table 1). The parameters, such as Fischer's test (F-value), the probability (p-value), correlation coefficient (R), coefficient of determination (R^2) were utilized to predict the show of the response of the esterification process. In addition, diagnostic plots, such as standardized residual and run number plot, expected normal value and residuals plot, studentized residuals and predicted values plot, predicted values and real values plot were also employed to estimate of the model. The second order polynomial regression model equation is generally indicated as in Eq. (3).

$$Y = \beta_o + \sum_{i=1}^{4} \beta_i X_i + \sum_{i=1}^{3}\sum_{j=i+1}^{4} \beta_{ij} X_i X_j + \sum_{i=1}^{4} \beta_{ii} X_i^2 \quad (3)$$

Herein, Y is the predicted response (FFA conversion); β_o, β_i, β_{ii}, β_{ij} are the regression coefficients (β_o is the constant term, β_i is a linear term, β_{ii} is a quadratic term and β_{ij} is an interaction term); X_i, X_j are coded independent factors.

Table 2. The coded independent factors, experimental results and predicted values

Run	Independent Variables				FFA conversion (%)			Run	Independent Variables				FFA conversion (%)		
	X_1	X_2	X_3	X_4	Experiment	Predict	Residual		X_1	X_2	X_3	X_4	Experiment	Predict	Residual
1	6.25	3.25	55	75	70.23	71.12	-0.89	16	8.75	7.75	65	105	94.98	94.17	0.81
2	8.75	3.25	55	75	66.89	68.39	-1.50	17	5	5.5	60	90	77.36	79.11	-1.75
3	6.25	7.75	55	75	88.45	86.47	1.98	18	10	5.5	60	90	85.83	82.21	3.62
4	8.75	7.75	55	75	82.69	85.15	-2.46	19	7.5	1	60	90	65.03	67.44	-2.41
5	6.25	3.25	65	75	80.32	79.52	0.80	20	7.5	10	60	90	98.06	93.79	4.27
6	8.75	3.25	65	75	79.45	76.65	2.80	21	7.5	5.5	50	90	76.55	74.87	1.68
7	6.25	7.75	65	75	83.79	85.12	-1.34	22	7.5	5.5	70	90	79.97	79.78	0.19
8	8.75	7.75	65	75	80.01	83.67	-3.66	23	7.5	5.5	60	60	86.51	85.31	1.20
9	6.25	3.25	55	105	74.23	72.36	1.87	24	7.5	5.5	60	120	97.71	97.05	0.66
10	8.75	3.25	55	105	78.17	76.92	1.25	25	7.5	5.5	60	90	79.66	78.77	0.89
11	6.25	7.75	55	105	88.80	91.68	-2.88	26	7.5	5.5	60	90	77.27	78.77	-1.50
12	8.75	7.75	55	105	95.07	97.66	-2.59	27	7.5	5.5	60	90	81.69	78.77	2.92
13	6.25	3.25	65	105	81.13	78.75	2.38	28	7.5	5.5	60	90	80.07	78.77	1.30
14	8.75	3.25	65	105	79.41	83.17	-3.76	29	7.5	5.5	60	90	75.54	78.77	-3.23
15	6.25	7.75	65	105	88.05	88.33	-0.28	30	7.5	5.5	60	90	78.38	78.77	-0.39

https://doi.org/10.52111/qnjs.2021.15309

Table 3. ANOVA results for the adjusted regression model

Source/Term	Degree of freedom (DF)	Coefficient	Sum of squares (SS)	Mean squares (MS)	F-value	P-value*	Remarks
Model	14		1751.0	125.07	12.84	<0.0001	Significant
β_o		80.76				0.55	Insignificant
Linear	4						
X_1	1	-13.04				0.224	Insignificant
X_2	1	11.32				0.04827	Significant
X_3	1	3.807				0.249	Insignificant
X_4	1	-2.777				0.00543	Significant
Square	4						
X_1^2	1	0.303				0.439	Insignificant
X_2^2	1	0.09109				0.451	Insignificant
X_3^2	1	-0.01440				0.555	Insignificant
X_4^2	1	0.01379				0.000106	Significant
Interaction	6						
X_1X_2	1	0.126				0.657	Insignificant
X_1X_3	1	-0.00550				0.965	Insignificant
X_1X_4	1	0.09723				0.03374	Significant
X_2X_3	1	-0.217				0.007	Significant
X_2X_4	1	0.02946				0.222	Insignificant
X_3X_4	1	-0.00667				0.531	Insignificant
Residual	15		146.10	9.740			
Lack of fit (LOF)	10		122.25	12.23	2.5636	0.155	Insignificant
Pure error	5		23.84	4.769			
Total	20		1897.1				
R^2: 0.923; adjusted R^2: 0.851; R^2 for prediction: 0.611							

**P-value < 0.05: statistically significant at the confident level of 95%*

3. RESULTS AND DISCUSSION

3.1. Regression model and statistical analysis for the FFA conversion in WCGO

The experimental and foreseen results of the FFA conversion in WCGOs were shown in Table 2. As per RSM, the full factorial CCD was utilized to fix the acquired data to Eq. (3). As the results, the best fit model was described in Eq. (4):

$$FFA\ Conversion\ (\%) = 11.32X_2 - 2.777X_4 + 0.01379X_4^2 + 0.09723X_1X_4 - 0.217X_2X_3$$

The ANOVA results for the adapted regression model were summarized in Table 3. The suitability of the designed model was evaluated as per F-value, P-value, R^2, and lack of fit (LOF).[7,8] At 95% confidence level, F-value and P-value were 12.84 and below 0.0001, respectively. Correlation coefficient, R^2, illustrated that 92.3% of the FFA conversion variation was influenced by independent variables as in Table 1. Only 7.7% of this variation was from randomly errors. Moreover, the LOF (0.155 > 0.05) shown that the LOF was not significant. These values indicated that model term are significant and suitable to forecast the FFA conversion in WCGO.

Also, as shown in Table 3, each term in the regression model was also evaluated to test how well the importance and its interconnection to the FFA conversion in WCGO. A P-value less than 0.05 shows that this term is significant. After withdrawing insignificant terms, by considering the linear, square, and interaction impacts, the linear term of H_2SO_4/WCGO catalyst content (X_2), and reaction time (X_4), the square term of reaction time (X_4^2), the interaction terms of X_1X_4 and X_2X_3 were significant (as in Eq. 4).

The residual plots were investigated for the model examining in Figure 1a – 1d. The standardized residuals plot for all tests were indicated in Figure 1a. It shows values between ±1.5 expressing that the estimation of the fixed model to the response was quite good.[6,8] The expected normal value and residual plot was utilized to express the issuing figure of the data (Figure 1b). This plot was almost linearly indicating that it was normally issued in the model response. The correlation between studentized residuals and predicted values specified that the points were under the meanwhile ±2.5 (Figure 1c). This designated that there was no need for variation of the response variable. The predicted values against real benefits were indicated clearly in Figure 1d. The data have linear conduct and are issued near diagonal line. Consequently, the obtained model is acceptable to predict the FFA conversion in WCGO via esterification reaction.

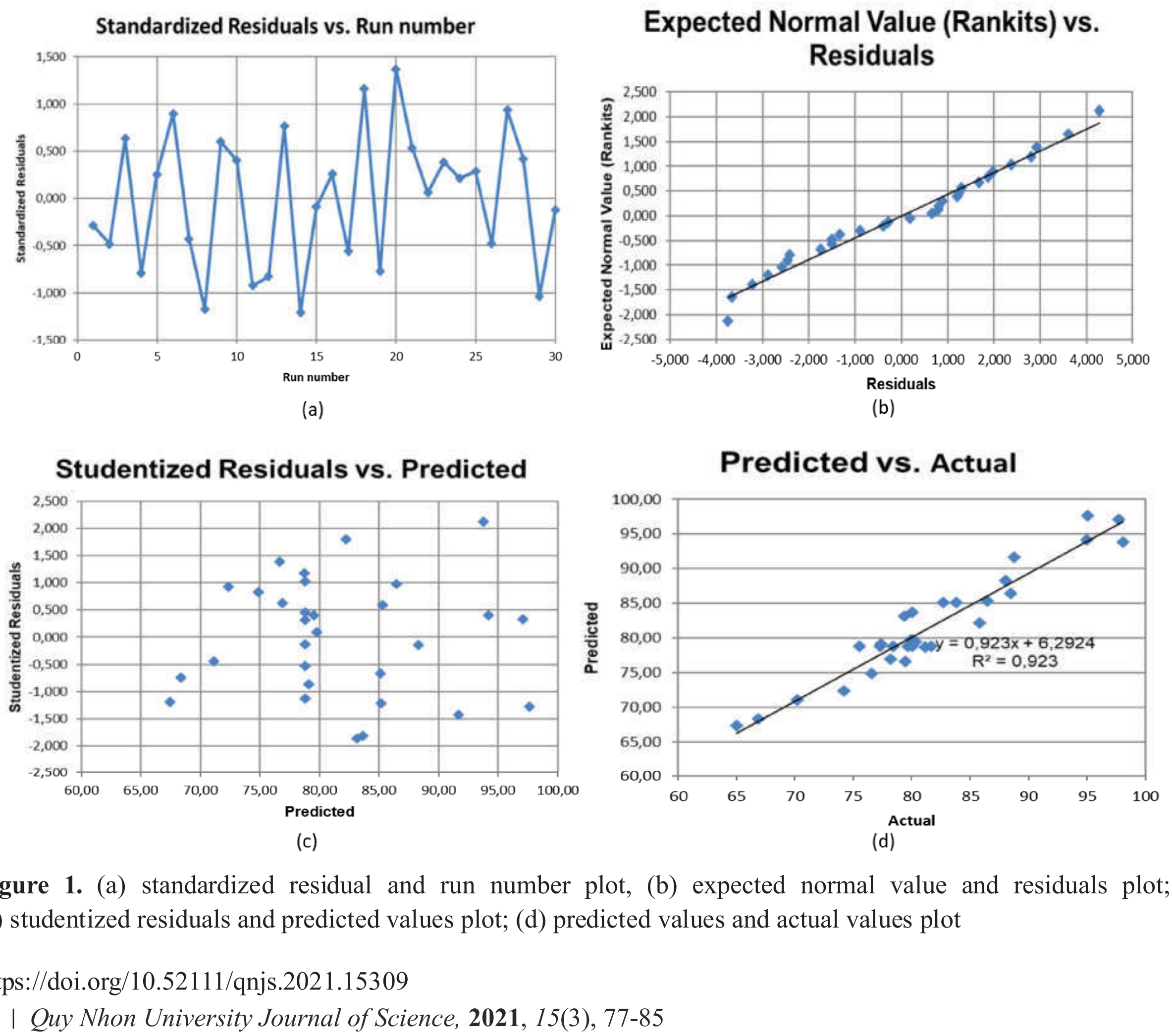

Figure 1. (a) standardized residual and run number plot, (b) expected normal value and residuals plot; (c) studentized residuals and predicted values plot; (d) predicted values and actual values plot

3.2. Interaction effects of the factors on the FFA conversion in WCGO

The impacts of the interaction factors were shown clearly in Figures 2a – 2f. The slope of the contour will decide the interaction's degree of this variable to FFA conversion in WCGO – the higher slope is the greater effect gets. The higher slope of the contour of the catalyst content indicated higher effect of this variable in comparison with the molar ratio (Figure 2a). Next, by using at least 1 wt.% of H_2SO_4 (to WCGO), FFA conversion clearly increase following the increasing of reaction temperature (Figure 2d). In addition, the slope of the catalyst content (Figure 2e) is higher the slope of the molar ratio (Figure 2c) at the same reaction time. Moreover, at the same temperature range, the FFA conversion can be up to 100% and 84% by using about 9 wt.% of catalyst content (Figure 2d) and 10 mol/mol (Figure 2b). These results proved the importance of H_2SO_4 catalyst on esterification reaction. Catalyst has a vital effect on the FFA conversion as detailed coefficients in Eq. (4). Hence, the enlargement of catalyst content expedites the speed of the conversion from FFA to esters (biodiesel). These results are consistent with the published results of the previous studies.[6,8]

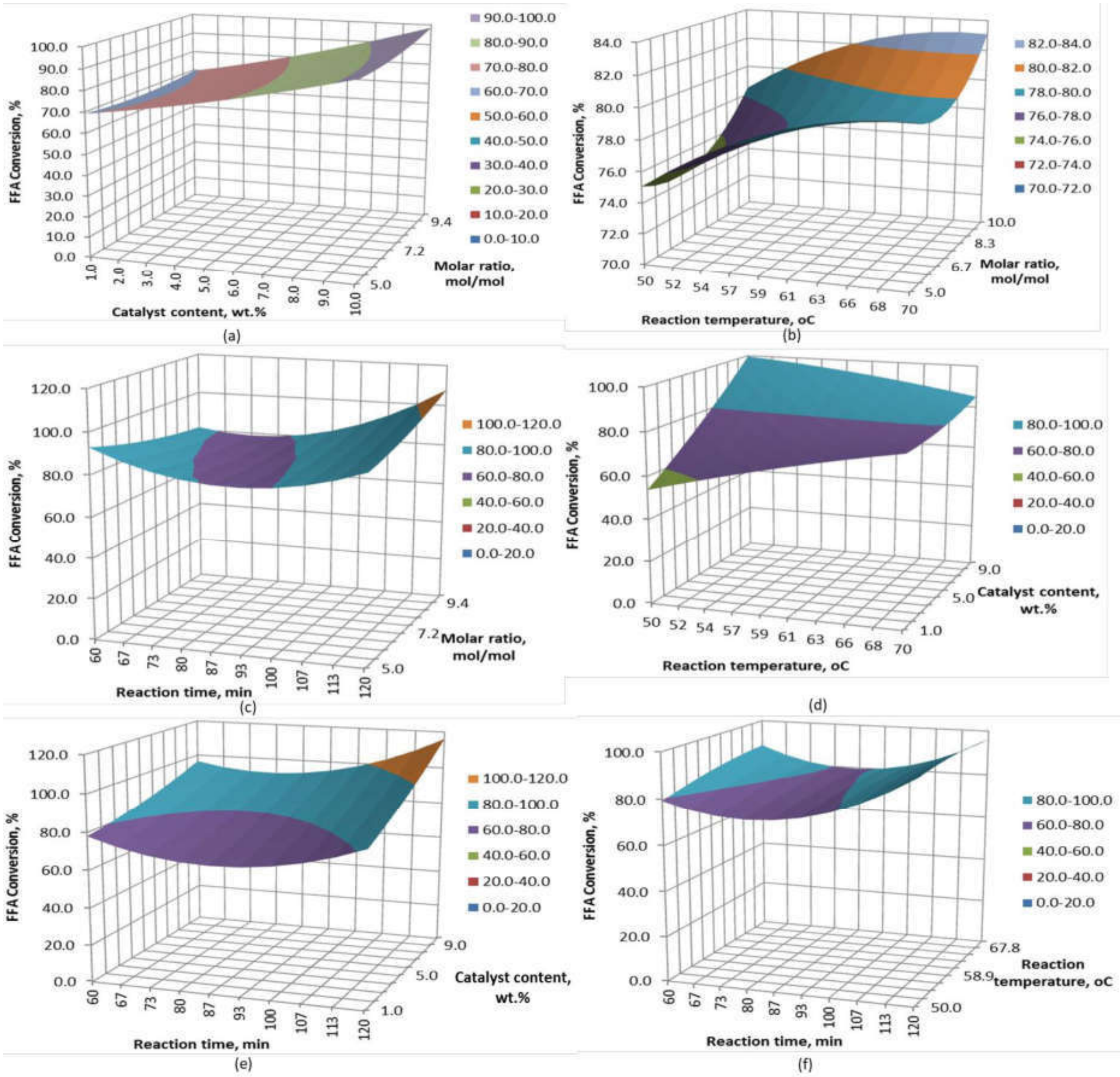

Figure 2. Interaction effects of the factors on FFA conversion in WCGO: (a) molar ratio and catalyst content, (b) molar ratio and reaction temperature; (c) molar ratio and reaction time; (d) catalyst content and reaction temperature; (e) catalyst content and reaction time; (f) reaction temperature and time

3.3. Optimization of variables for the FFA conversion in WCGO

The aim of this study is to reduce the FFA in WCGO as much as possible. Based on experimental results, the FFA conversion in WCGO changed from 65% to 98%, approximately. With the intial FFA content about 7 wt.%, the experimental condition to gain 90% of FFA conversion (final FFA content about 0.71 wt.%) were chosen to optimize via RSM. The optimum parameters were determined clearly, including the MeOH/WCGO molar ratio of 8.18 mol/mol, H_2SO_4/WCGO catalyst content of 8.74 wt.%, reaction temperature of 60 ^oC and reaction time of 90 min.

3.4. The fuel properties analysis of the final product

Some important properties of the esterified oil are shown in Table 4. Most of the properties of the final product met the limits according to standards of European Nations (EU), American Society for Testing and Materials (ASTM) as well as Vietnam (TCVN), except the viscosity at 40 ^oC. The reason for this problem is that the unsaturated fatty acids (palmitic acid, stearic acid) content in WCGO are quite high.[4,5] The viscosity of the unsaturated fatty acids increases following the decrease of the number of double bonds in the molecule. However, this problem can be solved in the coming stages of biodiesel production as well as in the blending with petroleum based diesel.

Table 4. Some properties of the esterified oil

Item	Property	Unit	Test method	Specification	Result
1	FFA content	wt.%	ASTM D664	≤ 1	0.71 ± 0.03
2	Density at 15 ^oC	kg/m^3	TCVN 6594 (ASTM D1298)	860 – 900	879 ± 5
3	Viscosity at 40 ^oC	cSt	ASTM D445	3.5 – 5.0	5.3 ± 0.2
4	Water content	wt.%	TCVN 2631-1993 (ASTM D2709)	≤ 0.05	0.045 ± 0.002
5	Carbon residue	wt.%	TCVN 6324 (ASTM D189)	≤ 0.3	0.29 ± 0.01
6	Sulfated ash	wt.%	EN 14538 (ASTM D874)	≤ 0.02	0.012 ± 0.002
7	Flash point	°C	TCVN 2699-1995 (ASTM D93)	≥ 130	152 ± 2

4. CONCLUSIONS

The conversion of FFA in WCGO by esterification using CCD based on RSM was evaluated. Some important conclusions are drawn as follows:

• The proposed model was applied to forecast the influence of variables to lessen the FFA content. The agreement of this model was demonstrated by a high correlation coefficients (R^2 = 0.923).

• The FFA content in WCO is decreased from 7 wt.% to 0.7 wt% and 90 % FFA conversion was reached, within the advisable standard to produce biodiesel (max 1 wt.% of FFA).

• The impact of experiment variables for the acid-catalyzed esterification was explored and optimized as per RSM, such as the MeOH/WCGO molar ratio, H_2SO_4/WCGO catalyst content, temperature and reaction time. RSM indicated that the catalyst content are the most important factor to the predicted model.

• Most of the properties of the final esterified oil adapt as per strictly standards. This may be a good cornerstone for the next stages of biodiesel production.

Acknowledgement: *This research is conducted within the framework of the student scientific research project for the academic year 2020 - 2021 under the project code S2020.657.21.*

REFERENCES

1. Dang Nguyen Thoai, C. Tongurai, K. Prasertsit, A. Kumar. Review on biodiesel production by two-step catalytic conversion, *Biocatalysis and Agricultural Biotechnology,* **2019**, *18*, 101023.

2. Z. Al-Hamamre, S. Foerster, F. Hartmann, M. Kröger, M. Kaltschmitt. Oil extracted from spent coffee grounds as a renewable source for fatty acid methyl ester manufacturing, *Fuel,* **2012**, 96, 70–76.

3. USDA Foreign Agricultural Service, Global Agricultural Information Network, Vietnam Coffee Annual 2019. Available online at https://asiacom.vn/vietnam-coffee-exports-under-the-top-2-of-the-world/.

4. D. R. Vardon, B. R. Moser, W. Zheng, K. Witkin, R. L. Evangelista, T. J. Strathmann, K. Rajagopalan, and B. K. Sharma. Complete utilization of spent coffee grounds to produce biodiesel, bio-oil, and biochar, *ACS Sustainable Chemistry & Engineering,* **2013**, 1, 1286–1294.

5. M. R. Marcelo de Melo, H. M. A. Barbosa, C. P. Passos, C. M. Silva. Supercritical fluid extraction of spent coffee grounds: Measurement of extraction curves, oil characterization and economic analysis, *The Journal of Supercritical Fluids,* **2014,** *86*, 150–159.

6. C. Mueanmasa, R. Nikhoma, J. Kaew-Ona, K. Prasertsit. Statistical optimization for esterification of waste coffee grounds oil using response surface methodology, *Energy Procedia,* **2017**, *138*, 235–240.

7. D. D. Steppan, J. Werner, R. P. Yeater. *Essential regression and experimental design for chemists and engineers,* Electronic Book, 1998.

8. Dang Nguyen Thoai, C. Tongurai, K. Prasertsit, A. Kumar. Predictive Capability Evaluation of RSM and ANN in Modeling and Optimization of Biodiesel Production from Palm (Elaeisguineensis) Oil, *International Journal of Applied Engineering Research,* **2018**, 13(10), 7529–7540.