PRODUCTION OF BIODIESEL FROM WASTE COOKING OIL USING SIMULTANEOUS ESTERIFICATION AND TRANSESTERIFICATION PROCESS: AN OPTIMIZATION STUDY BASED ON RESPONSE SURFACE METHODOLOGY

Dang Nguyen Thoai*, Nguyen Thi Thuy Hong

Quy Nhon University, Gia Lai, Vietnam

*Corresponding author: dangnguyenthoai@qnu.edu.vn

(Received: April 30, 2025; Revised: June 15, 2025; Accepted: June 18, 2025)

DOI: 10.31130/ud-jst.2025.23(9C).543E

Abstract - Waste cooking oil (WCO) is an abundant, low-cost feedstock for biodiesel, but its high free fatty acid (FFA) content challenges conventional base-catalyzed transesterification, often causing soap formation and low yield. This study investigates simultaneous esterification–transesterification of WCO to simplify the process and reduce cost. Response Surface Methodology (RSM) was applied to assess key variables - methanol-to-oil molar ratio, catalyst concentration, temperature, and reaction time - on biodiesel ester content. Optimal conditions were identified at a 4:1 methanol-to-oil ratio, 0.75 wt.% KOH, 65°C, and 60 minutes, yielding biodiesel with >96.5% ester content, meeting EN 14214 standards. These results confirm the feasibility of the integrated process and provide insights for efficient biodiesel production from high-FFA feedstocks.

Key words - Biodiesel; waste cooking oil; esterification; transesterification; response surface methodology

1. Introduction

The increasing global demand for sustainable and renewable energy sources has intensified interest in biodiesel as an eco-friendly alternative to petroleum-based diesel fuel. Biodiesel, composed of fatty acid alkyl esters, is typically produced via transesterification of triglycerides or esterification of free fatty acids (FFAs) using short-chain alcohols. It is biodegradable, emits fewer greenhouse gases, and is compatible with existing diesel engines-making it a valuable contributor to clean energy goals [1–3].

Among the various feedstocks available for biodiesel production, waste cooking oil (WCO) is particularly attractive due to its low cost, abundance, and potential to reduce environmental pollution. However, WCO often contains a high percentage of FFAs and moisture, which makes it unsuitable for direct alkaline-catalyzed transesterification. FFAs react with basic catalysts to form soaps, while water promotes hydrolysis of triglycerides, increasing the FFA content even further and reducing biodiesel yield and quality [5–8].

To overcome this limitation, a two-step production process has been proven effective: an acid-catalyzed esterification step to lower the FFA level below 1 wt.%, followed by a base-catalyzed transesterification step to convert triglycerides into methyl esters. This approach improves conversion efficiency and reduces soap formation.

This study focuses on optimizing reaction conditions for biodiesel production from WCO using simultaneous esterification and transesterification process. Employing Response Surface Methodology (RSM), the study investigates the influence of key parameters-such as alcohol-to-oil molar ratio, catalyst concentration, temperature, and reaction time-on methyl ester yield. The goal is to enhance process efficiency and reliability for industrial application using low-quality feedstocks.

2. Related works

Several researchers have addressed the technical challenges of converting high-FFA oils like WCO into biodiesel. Conventional single-step alkaline transesterification is unsuitable for such feedstocks due to excessive soap formation and poor product separation when FFA content exceed 1 wt.% [3, 5]. To resolve this, the two-step method-acid esterification followed by base transesterification-has been extensively studied.

Pioneering work by Canakci and Van Gerpen demonstrated the effectiveness of pre-esterification in reducing FFAs, enabling successful downstream conversion [6]. Likewise, Fukuda et al. highlighted pretreatment requirements for various oils and discussed catalytic systems [8]. Studies by Marchetti and Errazu, and Thoai et al. emphasized the use of sulfuric acid for FFA esterification, citing its compatibility with large-scale processes and high catalytic activity [5, 9].

The second step-alkaline transesterification-is well-established, with NaOH, KOH, and sodium methoxide commonly used in industry. Research by Thoai et al. explored key reaction variables (e.g., catalyst loading, methanol/oil ratio, temperature, time) and their influence on yield and ester content [10].

In terms of process optimization, statistical tools like Taguchi and RSM have been widely adopted [5, 7, 10, 11]. Among this, many researchers applied RSM to optimize biodiesel yield by modeling interactions among multiple parameters [5, 7, 10]. These studies confirmed RSM's utility in identifying optimal conditions and enhancing process efficiency.

While previous studies have laid a strong foundation for biodiesel production from high-FFA feedstocks, they often treat esterification and transesterification as isolated, sequential steps with separate optimization strategies. In contrast, this study introduces a novel approach by simultaneously optimizing both processes using RSM. By treating simultaneous esterification and transesterification

process as an integrated system, the research provides a more comprehensive understanding of parameter interactions, paving the way for a more efficient, unified, and scalable biodiesel production process tailored specifically for WCO.

3. Materials, experimental and statistical methods

3.1. Materials

Waste cooking oil (2.5 wt% of FFA) was obtained from the student's canteen at Quy Nhon University. Commercial grade methanol (MeOH, 99.8 wt% purity), sulfuric acid (H_2SO_4, 98% wt.%) and sodium hydroxide (NaOH, 99 wt% purity) were purchased from Binh Dinh Chemical and Scientific Equipment Co. Ltd., Vietnam.

3.2. Experimental and statistical methods

3.2.1. Study of the first step of esterification reaction

The esterification was conducted in a 0.5L three-neck flask chemically equipped for reflux and mixing. The scheme of equipment for experiment is shown in Fig 1. In accordance with previous studies [5], the reaction conditions studied were shown as follows:

- The molar ratio of MeOH/FFA: 40.11 mol/mol;
- The varying H_2SO_4/FFA content: 10.64 wt.%;
- The reaction temperature: 60°C;
- The reaction time: 5h.

After finish this stage, product was moved to the separating funnel and achieved in 90 min to separate into two phases of esterified oils (EO) and aqueous phase. The EO is feedstock for the transesterification reaction.

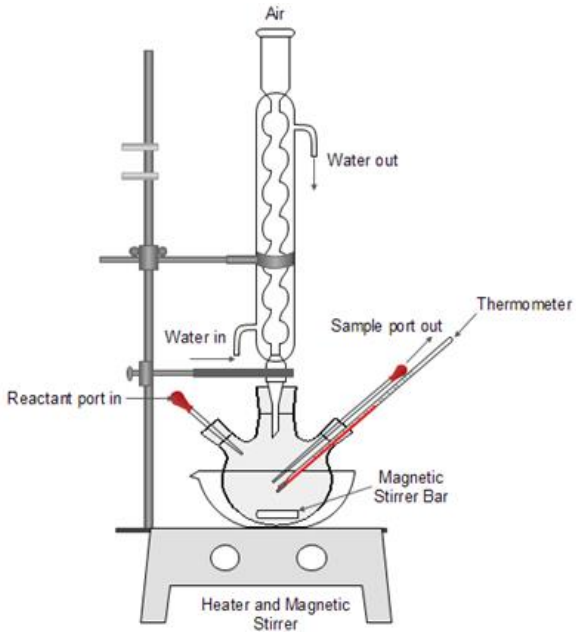

Figure 1. *The scheme of equipment for experiment*

3.2.2. Study of the second step of transesterification reaction

The transesterification was conducted in a schems similar to the esterification process. The reaction conditions studied were shown as follows:

- The molar ratio of MeOH/EO: 4.0-6.0 mol/mol;
- The varying KOH/EO content: 0.75-1.25 wt.%;
- The reaction temperature: 55 – 65°C;
- The reaction time: 40 – 60 min.

All the experiments have been carried out thrice to check errors. After finishing this process, the mixture was moved to the separating funnel and settled within 60 minutes to separate into two phases of methyl ester and glycerol phase. The methyl ester phase was washed by hot water (80°C) without and with shaking thrice to remove glycerol phase from methyl ester phase. The washed methyl ester was dried by the heating at 110°C within 90 min. Finally, the final biodiesel product was determined the ester content [14].

3.2.3. RSM statistical methods

Response Surface Methodology (RSM) is a powerful statistical tool commonly employed to explore the relationships between process variables and their effects on a response. In this research, RSM was utilized in conjunction with Minitab 18 to analyze experimental outcomes and guide optimization strategies. To find out the optimal conditions for achieving the desired methyl ester yield, the Box-Behnken Design (BBD) was implemented. BBD includes three coded levels for each factor (–1, 0, +1). The central points (coded as 0) were replicated to provide an estimate of pure error.

For this simultaneous esterification and transesterification process, four primary variables were selected as inputs: methanol-to-oil molar ratio (X_1), catalyst concentration (X_2), reaction time (X_3), and reaction temperature (X_4). The methyl esters content served as the response (output). Table 1 shows the experimental ranges and coded levels for each independent factor. A total of 28 experimental runs were conducted. The correlation between the selected reaction condition and the response was modeled using a second-order polynomial equation, which accounted for both linear and interaction terms. The mathematical equation of the second-order regression model used in this work is as follows:

$$Y = \beta_0 + \sum_{i=1}^{4} \beta_0 X_i + \sum_{i=1}^{3} \sum_{j=i+1}^{4} \beta_{ij} X_i X_j + \sum_{i=1}^{4} \beta_{ii} X_{ii} \quad (1)$$

where Y is the predicted response (methyl esters content); β_0, β_i, β_{ii}, β_{ij} are the regression coefficients (β_0 is referred to as 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.

4. Result analysis

4.1. RSM modeling for the transesterification process

Table 1 presents the number of experiments, experimental conditions, obtained results, and predicted values for the initial step of transesterification. The findings indicate that the ester content in this stage is influenced by four independent variables.

Table 1. *The coded independent factors, experimental results and predicted values of the transesterification process*

Number of run	Experimental condition				Ester content in biodiesel (%)		
	X_1	X_2	X_3	X_4	Experiment	Predict	Error
1	6	0.75	60	50	96.67	95.69	0.98
2	5	1.25	65	50	98.13	100	-1.87
3	5	1	60	50	95.67	97.27	-1.60
4	6	1	65	50	99.13	100	-0.87
5	5	1	65	40	97.31	95.44	1.87
6	4	1.25	60	50	92.4	91.88	0.52
7	5	1.25	60	60	97.13	96.31	0.82
8	4	1	55	50	91.58	91.45	0.13
9	5	0.75	65	50	95.04	94.99	0.04
10	4	1	60	60	92.4	93.33	-0.93
11	6	1	60	40	95.53	94.72	0.81
12	5	1.25	55	50	96.49	96.65	-0.16
13	6	1.25	60	50	98.49	96.43	2.06
14	4	1	65	50	97.31	95.27	2.04
15	4	1	60	40	83.4	84.61	-1.21
16	5	1	60	50	98.95	97.27	1.69
17	5	1.25	60	40	90.31	91.61	-1.30
18	5	0.75	55	50	96.49	94.68	1.81
19	5	1	60	50	98.13	97.27	0.86
20	5	0.75	60	60	93.95	94.03	-0.08
21	6	1	60	60	98.95	97.86	1.09
22	5	1	55	40	94.1	92.29	1.81
23	5	0.75	60	40	84.67	86.87	-2.20
24	5	1	60	50	96.31	97.27	-0.96
25	6	1	55	50	97.31	100	-2.69
26	4	0.75	60	50	85.03	85.59	-0.54
27	5	1	65	60	99.55	100	-0.45
28	5	1	55	60	99.13	99.51	-0.38

Table 2. *ANOVA results for the adjusted regression model for the transesterification process*

Source/ Terms	Degree of Freedom (DF)	Coefficient (β_i)	Adjusted Sum of Square (Adj SS)	Adjusted Mean of Square (Adj MS)	F-value	P-value*	Remark
Model	14		480.104	34.293	7.77	0	**Significant**
Constant		37				0.839	Not Significant
X_1	1	50.1	39.877	39.877	9.04	**0.01**	**Significant**
X_2	1	94.7	9.451	9.451	2.14	0.167	Not Significant
X_3	1	-8.3	15.296	15.296	3.47	0.085	Not Significant
X_4	1	4.43	31.142	31.142	7.06	**0.02**	**Significant**
X_1X_2	1	-5.55	7.701	7.701	1.74	0.209	Not Significant
X_1X_3	1	-0.196	3.822	3.822	0.87	0.369	Not Significant
X_1X_4	1	-0.14	7.784	7.784	1.76	0.207	Not Significant
X_2X_3	1	0.618	2.387	2.387	0.54	0.475	Not Significant
X_2X_4	1	-0.246	1.513	1.513	0.34	0.568	Not Significant
X_3X_4	1	-0.0129	1.664	1.664	0.38	0.55	Not Significant
X_1^2	1	-2.22	29.582	29.582	6.7	**0.022**	**Significant**
X_2^2	1	-42.3	41.989	41.989	9.51	**0.009**	**Significant**
X_3^2	1	0.0791	23.453	23.453	5.31	**0.038**	**Significant**
X_4^2	1	-0.0242	35.005	35.005	7.93	**0.015**	**Significant**
Error	13		57.372	4.413			
Lack-of-Fit (LOF)	10		50.328	5.033	2.14	**0.288**	**Not significant**
Pure Error	3		7.043	2.348			
Total	27		537..476				
R^2 = 89.33%; Adjusted R^2 = 77.83%							

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

The analysis of variance (ANOVA) results are presented in Table 2. The adequacy of the proposed model was evaluated using several statistical parameters, including the F-value, P-value, lack of fit (LOF), coefficient of determination (R^2), and adjusted R^2 [5, 6, 9]. An F-value of 7.7, accompanied by an extremely low P-value (0.0), suggests that the model is statistically significant at the 95% confidence level. Furthermore, the LOF value of 0.288, being substantially higher than 0.05, indicates that the lack of fit is not significant compared to the pure error [5, 7, 10, 11], which is favorable for the model's predictive capability. Regarding model validation, minimal difference between R^2 (89.33%) and adjusted R^2 (77.83%) supports the reliability and significance of the model, as large discrepancies between these values would otherwise indicate model inadequacy [5,11].

Based on the RSM, a mathematical relationship between the input factors and the output objective (methyl ester content in biodiesel) was established, as shown in Equation (2).

$$Y = 37 + 50{,}1X_1 + 94{,}7X_2 - 8{,}3X_3 + 4{,}43X_4 - 5{,}55X_1X_2 - 0{,}196X_1X_3 - 0.14X_1X_4 + 0{,}618X_2X_3 - 0{,}246X_2X_4 - 0{,}0129X_3X_4 - 2{,}22X_1^2 - 42{,}3X_2^2 + 0.0792X_3^2 - 0{,}02415X_4^2 \quad (2)$$

As illustrated in Table 2, each term within the refined regression model was examined to assess its statistical significance and its influence on the methyl ester content. A P-value below 0.05 indicates that the corresponding factor has a statistically significant effect. The analysis reveals that the MeOH/EO molar ratio and the KOH/EO catalyst concentration are the most influential variables in the combined esterification and transesterification process. According to the coefficients presented in Eq. (2), both the molar ratio and catalyst loading positively affect methyl ester yield, suggesting that increasing these parameters enhances the conversion rate from triglycerides to methyl esters. The final adjusted regression model, expressed in Eq. (3), includes only the significant variables, as those with P-values exceeding 0.05 were excluded. These findings are consistent with observations reported in prior research [10, 15–17].

$$Y = 37 + 50{,}1X_1 + 4{,}43X_4 - 2{,}22X_1^2 - 42{,}3X_2^2 + 0.0792X_3^2 - 0{,}02415X_4^2 \quad (3)$$

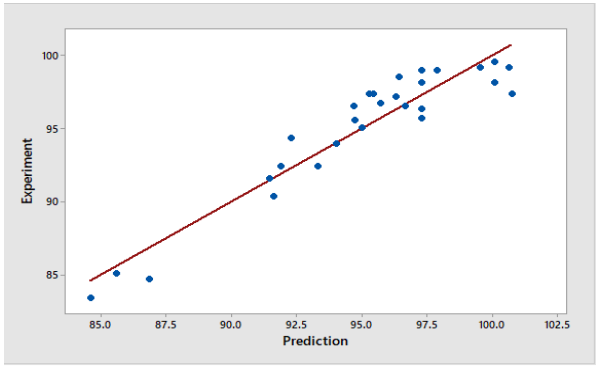

Figure 2. *Correlation between the experimentally obtained methyl ester content and the values predicted by the RSM model*

The correlation between the experimentally obtained methyl ester content and the values predicted by the RSM model is illustrated in Figure 2. The relationship curve is nearly linear, indicating the high accuracy of the proposed model developed using the RSM.

4.2. Interaction effects of the parameters

4.2.1. Interaction effects of the MeOH/EO molar ratio and other effects

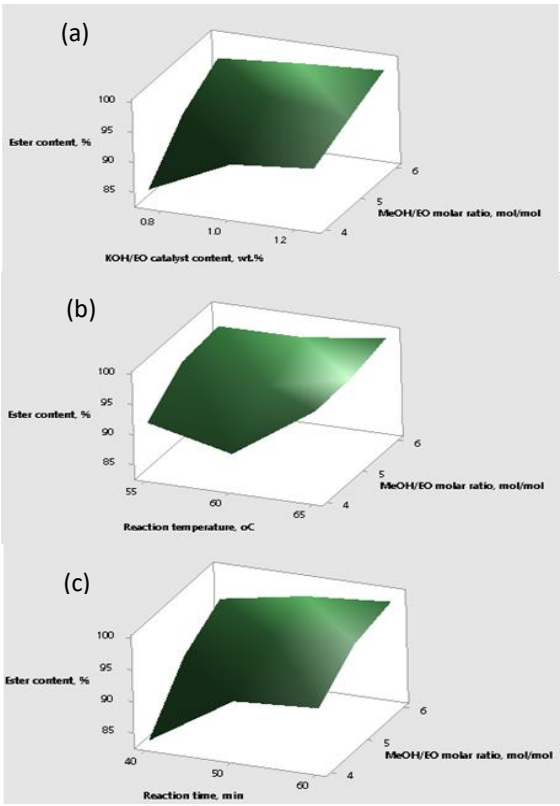

Figure 3. *Response surface plots for interaction effects of the MeOH/EO molar ratio with: (a) KOH/EO catalyst content, wt.%; (b) reaction temperature, °C and (c) reaction temperature, min*

In all three graphs (Figure 3 a-c), the surfaces are not flat or parallel to any one axis-instead, they show curved or sloped responses, indicating that the effect of the MeOH/EO molar ratio depends on the level of the other variable. Moreover the slope of the contours will decide the degree of the interaction of process factors to methyl esters content. The higher slope of the contour of the MeOH/EO molar ratio indicates great influence of this variable in comparison with other varibales. The similar conclusion can be seen in some previous results [5,10,15].

4.2.2. Interaction effects of the KOH/EO catalyst content and other effects

The surface plots presented in Figure 4(a-b) illustrate the impact of catalyst content, reaction temperature, and reaction time on ester content during biodiesel production. Based on the steepness of the slopes, catalyst content appears to be the most influential factor in both plots. As catalyst content increases, there is a marked rise in ester yield, indicating its pivotal role in accelerating the conversion process.

In the Figure 4a, reaction temperature also contributes positively to ester content, although the response surface indicates a more moderate gradient. This suggests that while temperature is an important factor, its influence is less significant than the catalyst content. Furthermore, the observed plateau at elevated temperatures implies a thermal threshold beyond which further increases yield diminishing returns.

In the Figure 4b, reaction time shows a relatively gentler slope compared to catalyst content, implying a weaker effect. While longer reaction times do improve ester content, the benefit diminishes beyond a certain point, likely due to the reaction reaching equilibrium.

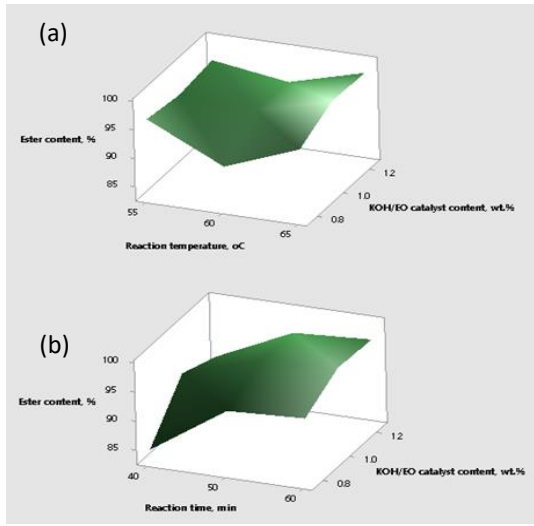

Figure 4. *Response surface plots for interaction effects of the KOH/EO catalyst content with: (a) reaction temperature, °C and (b) reaction temperature, min*

4.3. Optimization of process factors for production of biodiesel

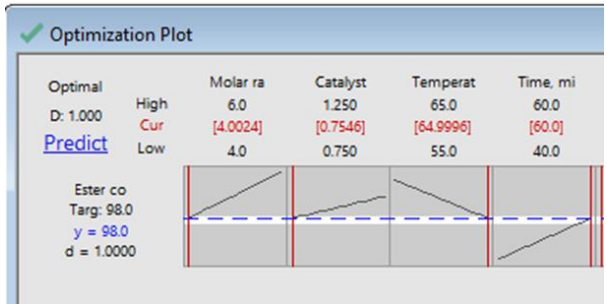

Figure 5. *Optimal condition of process factors for biodiesel production*

In process engineering, optimization refers to the structured identification of ideal operational conditions that achieve the desired output or system performance. In the context of biodiesel production, it entails identifying the optimal combination of reaction parameters that enhance conversion efficiency while maintaining fuel quality within standard specifications. In this study, numerical optimization was applied to refine the key operational variables using the response optimizer integrated in Minitab software (version 18). This statistical approach enables the prediction and adjustment of factor levels to achieve target responses based on regression

models developed through experimental data. The optimal conditions established for attaining a methyl ester content of 98% included a methanol-to-oil (MeOH/EO) molar ratio of 4.0, a catalyst loading (KOH/EO) of 0.75 wt.%, a reaction temperature of 65°C, and a reaction time of 60 minutes. These parameters reflect a carefully tuned balance that facilitates effective simultaneous esterification and transesterification process while minimizing side reactions and resource usage.

5. Conclusion

This study demonstrates the effectiveness of a simultaneous esterification and transesterification approach for biodiesel production from high-FFA WCO. By applying RSM for process optimization, key reaction parameters were identified that enable the efficient conversion of WCO into biodiesel with ester content exceeding 96.5%, thereby meeting established international quality standards. The optimized conditions-comprising a MeOH/EO molar ratio of 4:1, 0.75 wt.% KOH/EO catalyst loading, a reaction temperature of 65 °C, and a reaction time of 60 minutes-highlight the feasibility of this simultaneous esterification and transesterification process for treating complex feedstocks. This integrated strategy offers a practical and scalable solution for valorizing waste oils, contributing to the advancement of sustainable biofuel technologies.

REFERENCES

[1] I. Tariq, M. Zubair, W. Iqbal, A. Badshah, S. M. Abbas, and A. Haider, "Alkaline earth metal oxides supported on WO3@MCM-41; bifunctional catalysts for biodiesel production from corn and waste cooking oil", *Hybrid Advances,* vol. 10, 100477, 2025. https://doi.org/10.1016/j.hybadv.2025.100477

[2] A. Ahmad and M. I. Jilani, "Recent Advancements in catalysis used for biodiesel production: A review", *International Journal of Chemical and Biochemical Sciences (IJCBS),* vol. 25, no. 17, pp. 142-157, 2024.

[3] D. N. Thoai, C. Tongurai, K. Prasertsit, and A. Kumar, "Review on biodiesel production by two-step catalytic conversion", *Biocatalysis and Agricultural Biotechnology*, vol. 18, 101023, 2019. https://doi.org/10.1016/j.bcab.2019.101023

[4] C. M. Agu, K. A. Ani, O. N. Ani, P. C. Nnaji, C. H. Kadurumba, and C. Esonye, "Application of efficient soft computing approaches for modeling methyl ester yield from Azadirachta Indica (Neem) seed oil: A comparative study of RSM, ANN and ANFIS", *Green Technologies and Sustainability,* vol. 2, 100057, 2024. https://doi.org/10.1016/j.grets.2023.100057

[5] D. N. Thoai, P. T. L. Hang, and D. T. Lan, "Pre-treatment of waste cooking oil with high free fatty acids content for biodiesel production: An optimization study via response surface methodology*", Vietnam J. Chem*., vol. 57, no. 5, pp. 568-573, 2019. https://doi.org/10.1002/vjch.201900072

[6] M. Canakci and J. Van Gerpen, "Biodiesel production from oils and fats with high free fatty acids", *American Society of Agricultural Engineers,* vol. 44, no. 6, pp. 1429–1436, 2021.

[7] A. Buasri, C. Unkaew, P. Sawatkoed, P. Pipattananchaiyanan, and V. Loryuenyong, "Application of response surface methodology for optimization of biodiesel production parameters from waste vegetable oil using N-(2-hydroxy) propyl-3-trimethyl ammonium chitosan chloride-based catalyst", *South African Journal of Chemical Engineering,* vol. 47, pp. 50–59, 2024. https://doi.org/10.1016/j.sajce.2023.10.004

[8] Hidekl Fukuda, Akihiko Kondo, and Hideo Noda, "Biodiesel Fuel Production by Transesterification of Oils", *Journal of bioscience and bioenginneering,* vol. 92, no. 5, pp. 405-416, 2001. https://doi:10.1016/j.biombioe.2008.01.001

[9] J.M. Marchetti and A.F. Errazu, "Esterification of free fatty acids using sulfuric acid as catalyst in the presence of triglycerides", *Biomass and Bioenergy*, vol. 32, pp. 892 – 895, 2008.

[10] D. N. Thoai, C. Tongurai, K. Prasertsit, and A. Kumar, "A novel two-step transesterification process catalyzed by homogeneous base catalyst in the first step and heterogeneous acid catalyst in the second step", *Fuel Processing Technology*, vol. 168, pp. 97–104, 2017. http://dx.doi.org/10.1016/j.fuproc.2017.08.014

[11] A.O. Etim and P. Musonge, "The potential of waste avocado–banana fruit peels catalyst in the transesterification of non-edible Mafura kernel oil: Process optimization by Taguchi", *Cleaner Chemical Engineering*, vol. 11, 100158, 2025. https://doi.org/10.1016/j.clce.2025.100158

[12] N. Ghosh, M. Patra and G. Halder, "Current advances and future outlook of heterogeneous catalytic transesterification towards biodiesel production from waste cooking oil", *The Royal Society of Chemistry*, 2024. https://doi.org/10.1039/d3se01564e

[13] U. Bello, N. A. Amran, M. S. H. Ruslan, E. H. Yánez, U. Suparmaniam, H. Adamu, S. I. Abba, U. I. Tafida, and A. A. Mahmoud, "Enhancing oxidative stability of biodiesel using fruit peel waste extracts blend: Comparison of predictive modelling via RSM and ANN techniques", *Results in Engineering*, vol 21, 101853, 2024. https://doi.org/10.1016/j.rineng.2024.101853

[14] D. N. Thoai, S. Photaworn, A. Kumar, K. Prasertsit, and C. Tongurai, "A novel chemical method for determining ester content in biodiesel", *Energy Procedia,* vol. 138, pp. 536-543, 2018. https://doi.org/10.1016/j.egypro.2017.10.156

[15] H. Hamze, M. Akia, and F. Yazdani, "Optimization of biodiesel production from the waste cooking oil using response surface methodology", *Process Safety and Environmental Protection*, vol. 94, pp. 1–10, 2015. http://dx.doi.org/10.1016/j.psep.2014.12.005

[16] A. Bouaid, M. Martinez, and J. Aracil, "A comparative study of the production of ethyl esters from vegetable oils as a biodiesel fuel optimization by factorial design", *Chemical Engineering Journal*, vol. 134, pp. 93–99, 2007. https://doi.org/10.1016/j.cej.2007.03.077

[17] X. Yuan, J. Liu, G. Zeng, J. Shi, J. Tong, and G. Huang, "Optimization of conversion of waste rapeseed oil with high FFA to biodiesel using response surface methodology", *Renewable Energy*, vol. 33, pp. 1678–1684, 2008. https://doi.org/10.1016/j.renene.2007.09.007