

REACTIVE EXTRACTION SOXHLET-INTENSIFIED THE DIRECT BIODIESEL PRODUCTION OF WET SPENT COFFEE GROUND BIOMASS USING HETEROGENEOUS CATALYST

J. Br. Tarigan, M. Ginting, E. H. Sinaga and E. K. Sitepu✉

Department of Chemistry, Universitas Sumatera Utara, Medan 20155, Indonesia

✉Corresponding Author: ekositepu@usu.ac.id

ABSTRACT

Waste spent coffee ground (SCG) has a potential lipid to use for biodiesel production. One-pot simultaneous extraction and transesterification of SCG lipid using soxhlet apparatus were developed with heterogeneous substance as the catalyst. A response surface methodology based on the Box-Behnken design experiment was established to study the effect of catalyst weight (1 – 9 wt.%), ratio methanol: hexane (1:1 – 1:5, v/v) and reaction time (30 – 90 min). The quadratic equation model generated from the design was used to predict the optimum condition and it verified by experiment. The optimum biodiesel conversion of 36% occurred using CaO as catalyst under reaction condition at the maximum level of parameters while the conversion of 90% obtained using BaO in reaction condition of catalyst weight 6.5 wt%, a ratio of 1:5 and 30 minutes reaction time. In addition, the reactive extraction soxhlet (RES) intensified the DT of wet SCG biomass required simple phase separation and evaporation of co-solvent to purify the biodiesel product.

Keywords: Soxhlet, Direct Transesterification, Spent Coffee Ground, Biodiesel.

RASĀYAN J. Chem., Vol. 14, No.4, 2021

INTRODUCTION

One major problem in biodiesel low sales is its higher price than petroleum-derived diesel fuel.¹ The production cost of 75 – 88%, which is associated with purchasing the oil as raw material in biodiesel production^{2,3} is the reason. Therefore direct transesterification (DT) of oil-bearing materials has been proposed to reduce the cost. In fact, the DT-biodiesel product was met the international standard and could run the diesel engine.⁴ In the DT process, methanol acts as an extraction and reagent agent to simultaneously extract the oil and convert it to fatty acid methyl ester (biodiesel) with or without a catalyst.^{1,5} Non-catalytic DT offers some advantages, including high yield, purer and easy separation of product.⁶ However, the process has to be conducted at high temperature and pressure, requiring specific equipment and safety health concerns.⁷ In contrast, the catalytic DT process mainly operates in ambient pressure and temperature and could be intensified using some instrument such as ultrasonic, microwave, turbo thin-film device and more.^{1,5,8,9} Homogeneous catalysts, particularly alkaline bases, have better catalytic activity than acid, which therefore has been implemented in most biodiesel plants.¹⁰ However, those processes consume a lot of water for neutralization and purification of products which raises environmental issues related to disposal waste basic stream.^{1,11}

Heterogeneous catalyst provides some advantages, such as being recoverable and reusable.¹²⁻¹⁴ Simple filtration could separate the catalyst from the product as they have a different phase.^{11,12} However, this benefit generates mass transfer limitation as diffusion of the catalyst is limited, rendering low catalytic activity than homogeneous.¹⁵ Moreover, an excessive alcohol amount is required to avoid product adhering to the catalyst surface which could reduce its activity.⁷ However, alkaline earth such as SrO and BaO showed high catalytic activity on transesterification reaction. For example, previously studied on transesterification of sunflower oil using barium hydroxide has concluded that the heterogeneous catalyst has similar catalytic activity performance with potassium hydroxide.¹⁶ However leaching problem limited the utilization of those heterogeneous catalysts.¹⁷ Despite the low catalytic activity of SrO and BaO, CaO has low solubility in methanol, abundant either in nature or waste product and high biodiesel yield. For

example, a yield of 95% occurred after 3 hours transesterification reaction of soybean oil using CaO as the catalyst.¹⁸ Moreover, CaO derived from waste eggshell have been applied as a catalyst in the DT of dry microalgae *Acutodesmus obliquus* biomass yielding 86% biodiesel in 3.6 hours reaction time.¹⁹ However, the separation of heterogeneous catalyst from the seed/biomass is impossible as they stick together, hindering the reuse of the catalyst.²⁰ To solve the problem, impregnating the catalyst with ferric ion could increase the reusability of the catalyst.¹⁰ However, incorporation catalyst with a magnetic core required several reaction steps and various reagents.²¹

Our previous research has utilized soxhlet extraction in the DT of wet spent coffee ground (SCG). A Simultaneously extraction-transesterification reaction is occurred producing biodiesel in 30 minutes with a conversion efficiency of 97% using homogeneous alkaline as a catalyst. No effect of water contained in wet SCG was observed in biodiesel conversion efficiency as the extraction and transesterification proceeded in different chambers.²² Therefore, to add new insight in the reactive extraction soxhlet (RES) method, the heterogeneous catalyst is used to catalyse the transesterification reaction. Heterogeneous substances such as CaO and BaO were studied and compared their performance in the DT of wet SCG using RES method. A response surface methodology with Box-Behnken design experimental consist of three levels and three parameters was used to identify the optimum condition for biodiesel production. The parameter factors of catalyst weight, ratio methanol to hexane and reaction time were measured with biodiesel conversion as an independent parameter. The range of three levels for each factor was selected based on our previous studies.

EXPERIMENTAL

Materials

The SCG was gathered from the local coffee shop in Medan, Indonesia while all the chemicals used in this experiment were purchased and used without prior treatment. The catalysts used in this study (CaO and BaO) were purchased from local chemical dealer and was used as received.

The RES-intensified the DT of SCG using Heterogeneous Catalyst

The soxhlet apparatus which consists of two connected chambers were used for this experiment. The top chamber was filled with 10 gram of wet SCG in a thimble and connected to the condenser. In the second chamber, 150 ml of methanol and hexane as co-solvent was poured and the heterogeneous catalyst, either CaO or BaO was added based on the investigated weight of the catalyst. The reaction time counted when the solvents from the top chamber dropped down to the second chamber until the examined time. Next, the hexane layer was separated and evaporated to have biodiesel. The product was stored in a desiccator before gas chromatography (GC) analysis.

The Experimental Design

The optimum condition of the DT of wet SCG biomass was determined using Box-Behnken response surface methodology experiment design with three parameters and 3 levels. The experimental design comprised of 15 experiments to each heterogeneous catalyst with 3 replicates at the centre point. The biodiesel conversion (%) based on GC analysis was used as the response. The range of three levels of parameters was selected based on our previous research (Table-1).²²

Table-1: Reaction Condition of the DT wet SCG Biomass to Biodiesel

Parameters	Symbols	Levels		
		-1	0	1
Catalyst Weight (wt.%)	A	1	5	9
Ratio Methanol : Hexane (v/v)	B	1	3	5
Reaction Time (min)	C	30	60	90

The Box-Behnken design enables the determination of the single effect of each parameter and the interaction between them on the dependent variable. The quadratic equation model for predicting the optimum condition of the DT of wet SCG biomass to biodiesel using heterogeneous catalyst was expressed based on eqn.-1.

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{11}X_1^2 + a_{22}X_2^2 + a_{33}X_3^2 + a_{12}X_1X_2 + a_{13}X_1X_3 + a_{23}X_2X_3 + e \quad (1)$$

Where Y = the response (biodiesel conversion); a_0 is a constant; a_1 , a_2 , and a_3 are linear coefficients; a_{11} , a_{22} , and a_{33} are quadratic coefficients; a_{12} , a_{13} , and a_{23} are interaction coefficients; and X_1 , X_2 and X_3 , are the coded parameters such as catalyst weight (wt.%), ratio methanol: hexane (v/v) and reaction time (min), respectively. A total of 15 experimental conditions for both CaO and BaO as heterogeneous catalyst were studied to determine the quadratic equation as shown in Table-2.

Table-2: Experimental Design based on Box-Behnken Model of Three Parameters and Three Levels on the Biodiesel Conversion and Predicted Value.

Run	A	B	C	CaO		BaO	
				Biodiesel Conversion (%)	Predicted Values	Biodiesel Conversion (%)	Predicted Values
1	9	3	90	26.38	31.894	84.77	83.151
2	9	5	60	38.94	32.834	71.61	78.119
3	9	1	60	28.65	23.856	85.3	87.221
4	9	3	30	20.75	26.136	91.05	84.239
5	1	3	90	35.11	29.724	65.72	72.531
6	1	3	30	30.94	25.426	67.28	68.899
7	1	1	60	18.79	24.896	75.28	68.771
8	1	5	60	24.12	28.914	72.53	70.609
9	5	5	30	20.96	21.680	88.73	89.032
10	5	1	90	20.93	20.210	94.24	93.937
11	5	5	90	31.04	31.633	83.22	78.330
12	5	1	30	20.7	20.108	75.8	80.690
13	5	3	60	23.41	27.747	85.77	85.660
14	5	3	60	28.73	27.747	76.83	85.660
15	5	3	60	31.1	27.747	94.38	85.660

Biodiesel Conversion Analysis

Determination of biodiesel conversion was performed using GC analysis following EN 14103:2011 standard. Methyl heptadecanoate was used as an internal standard and added to the biodiesel sample. An aliquot of that mixture was injected into the GC apparatus (Shimadzu type 2010) consisting of a capillary column (length 15 mm and ID = 0.25 mm) and a flame ionization detector. The biodiesel conversion is expressed as C (in percentage) and was calculated based on the differences in the peak area of the methyl esters and internal standard as shown in eqn.-2.²³

$$C = \frac{\Sigma A - A_s}{A_s} \times \frac{C_s V_s}{m} \times 100\% \quad (2)$$

Where ΣA is the sum of methyl esters peak area and A_s is peak areas of internal standard, while C_s and V_s are the concentration and volume of internal standard, respectively and m is the mass of methyl ester sample.

RESULTS AND DISCUSSION

The water content of wet SCG biomass determined using the gravimetric method was 60%, while oil content was 12.5% based on dry biomass established using the soxhlet extraction method. The linoleic acid was dominated the fatty acid content in SCG oil, followed by palmitic acid. This result is in agreement with our previous investigation and other published results.^{22,24-26} The RES-intensified DT of wet SCG biomass using homogeneous alkaline base catalyst revealed that 30 minutes was sufficient to extract and convert the lipid to biodiesel while hexane was the best co-solvent to extract the lipid in the first chamber and deliver to the second chamber for transesterification reaction.²² Due to this, the level of reaction time was determined from 30 to 90 minutes while the effect of the ratio methanol to hexane as co-solvent was studied in a range ratio of 1:1 to 1:5. A review on CaO as a promising heterogeneous

catalyst in biodiesel production showed that the catalyst loading (wt.% based on palm oil) was varied and a 1% catalyst weight could convert 94% of biodiesel.¹⁷ Therefore, the catalyst weight in this study was set to 1% as the minimum point and 9% as the maximum point.

Optimization of the DT of Wet SCG Biomass using CaO as the Catalyst

The optimization of the DT of wet SCG biomass using CaO as catalyst was determined based on the single and interaction of parameters of catalyst weight, ratio methanol to hexane and reaction time. The experimental and predicted biodiesel conversions based on the Box-Behnken design experiment are shown in Table-2. The predicted biodiesel conversion was calculated based on the quadratic model developed from the experimental as presented in eqn.-3.

$$\text{Biodiesel Conversion (\%)} = 27.75 + 0.72 * A + 3.25 * B + 2.51 * C + 1.24 * AB + 0.37 * AC + 2.46 * BC + 2.38 * AA - 2.50 * BB - 1.83 * CC \quad (3)$$

Where A, B and C are the symbol of parameters as depicted in Table-1.

Analysis variance (ANOVA) of parameter and the correlation analysis on the biodiesel conversion of the RES-intensified DT of wet SCG biomass using CaO as catalyst was confirmed that no significant effect of the parameter. The F- and p-values of the quadratic model were 0.47 and 0.85, respectively, indicating that the model developed from this experiment is not significant as the p-value > 0.005. Moreover, the correlation coefficient (R^2) is quite low (0.46), indicating a moderate linear correlation between parameters.

The interaction effect of parameters on the biodiesel conversion was predicted as shown in the response surface plot in Fig.-1. Evidently, in Fig.-1A that higher catalyst loading in increasing ratio of methanol to hexane could increase the biodiesel conversion. The same trend is observed in figure 1B as increasing catalyst weight raises the biodiesel conversion in prolonged reaction time. This result supports the previously published research, which found that increasing catalyst loading on the reaction mixture increases biodiesel conversion.²⁷ However, in contrast, that previous result observed a catalyst agglomeration rendering decreasing biodiesel conversion while it did not occur in this study due to co-solvent used. Furthermore, the positive effect of catalyst loading can be identified from the quadratic eqn.-3 that both single and factorial for catalyst weight has positive sign meaning increasing this parameter could increase the biodiesel conversion.²⁸ Figure 1C showed the interaction between the ratio methanol : hexane and reaction time. It can be observed that the addition of hexane as a co-solvent intensifies the biodiesel conversion in increasing reaction time. However, this result does not support our previous studies which concluded that increasing co-solvent decrease the biodiesel yield.²² This could be because an excess of co-solvent causing less contact of the homogeneous catalyst to the SCG oil while it did not occur in this study as heterogeneous catalyst did not dissolve in methanol.²⁹

The optimum biodiesel conversion of 36% occurred using CaO as catalyst under reaction condition at the maximum level of parameters. The 100% biodiesel conversion could not be achieved using the level set up in this study as the quadratic regression model shown that all parameters have a positive effect on it. Based on that the predicted biodiesel conversion of ~99% could be accomplished using parameter values beyond the level set up, which is catalyst weight of 23 wt.%, ratio methanol : hexane of 1:7.5 and reaction time of 150 min.

Optimization of the DT of Wet SCG Biomass using BaO as the Catalyst

Response surface method using Box-Behnken design experiment which consists of 15 experimental conditions was conducted at random orders for optimization of the DT of wet SCG biomass using BaO as heterogeneous catalyst. Table-2 presents the biodiesel conversion based on experimental results and predicted conversion calculated from the quadratic regression equation.

$$\text{Biodiesel Conversion (\%)} = 85.66 + 6.49 * A - 1.82 * B + 0.64 * C - 2.74 * AB - 1.18 * AC - 5.99 * BC - 8.89 * AA - 0.59 * BB + 0.43 * CC \quad (4)$$

As shown in eqn.-4, the ratio of methanol to hexane has a negative effect on biodiesel conversion, while the interaction and factorial effect of all parameters also have negative signs except for the factorial of reaction time parameter. Furthermore, the ANOVA resulted in no significant effect for the model with F-

and p-value of 1.192 and 0.4457, respectively. The moderate linear correlation observed in this study as the correlation coefficient is 0.68.

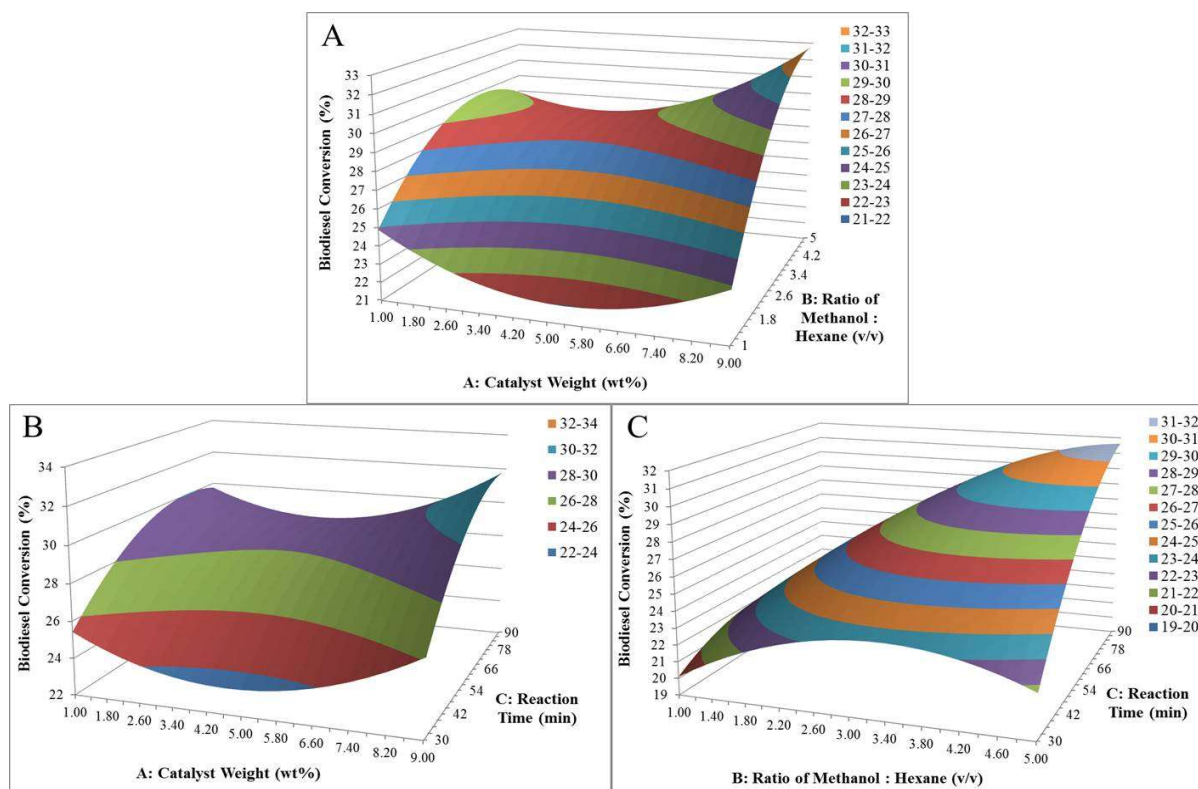


Fig-1: Response Surface Graphics of (A) Catalyst Weight and Ratio Methanol to Hexane; (B) Catalyst Weight and Reaction Time; and (C) Ratio Methanol to Hexane and Reaction Time on Biodiesel Conversion of the RES-intensified DT of wet SCG Biomass using CaO Catalyst.

Figure-2 shows the 3-dimensional response surface plot based on the quadratic model equation to investigate the interaction effect of variables for optimum condition determination. As shown in figure 2A, at all ratios of methanol to hexane, the biodiesel conversion was increased in increasing of catalyst weight and decreased after reaching the peak in excess of catalyst. This result in agreement with the previously published report which observed decreasing 7% of biodiesel yield in the overage of catalyst loading.³⁰ Ezzah-Mahmudah et al. reported the same result in transesterification waste cooking oil using $\text{Fe}_2\text{O}_3/\text{CaO}$ as the catalyst.²⁷ It concluded that the decreasing biodiesel yield was due to the increasing reaction mixture viscosity. A similar plot pattern was also observed in the interaction of catalyst weight and reaction time (Fig.-2B). Reaction time did not have any significant effect on biodiesel conversion in RES-intensified the DT of wet SCG biomass using BaO as a catalyst. In all catalyst weight, the biodiesel conversion tends similar in increasing reaction time. The interaction effect of the ratio methanol to hexane and reaction time was depicted in Fig.-2C. At a reaction time of 30 min, the biodiesel conversion was raised in increasing of ratio methanol to hexane and in was inclined ~10% in the prolonged reaction time. In contrast, at a high ratio of methanol to hexane, the biodiesel conversion was declined in increasing reaction time. It is presumably due to the transesterification reaction achieving equilibrium state at 30 mins reaction time and the biodiesel conversion decline as the reaction shift to the left in prolonged reaction time.³¹

Based on the quadratic equation model for RES-intensified the DT of wet SCG biomass using BaO as a catalyst, the optimum biodiesel conversion of 90% obtained in reaction condition of catalyst weight 6.5 wt.%, ratio methanol to hexane of 1:5 and reaction time of 30 min.

As predicted BaO has better catalytic activity in the DT of wet SCG than CaO. The sequence basicity of metal oxide follows the order of $\text{MgO} < \text{CaO} < \text{SrO} < \text{BaO}$.^{32,33} The result is in agreement with the

previous researcher which obtain biodiesel yield of 95.2% using BaO compare to 77.3% using CaO as catalyst in ultrasonic intensified the transesterification of palm oil to biodiesel.³⁴

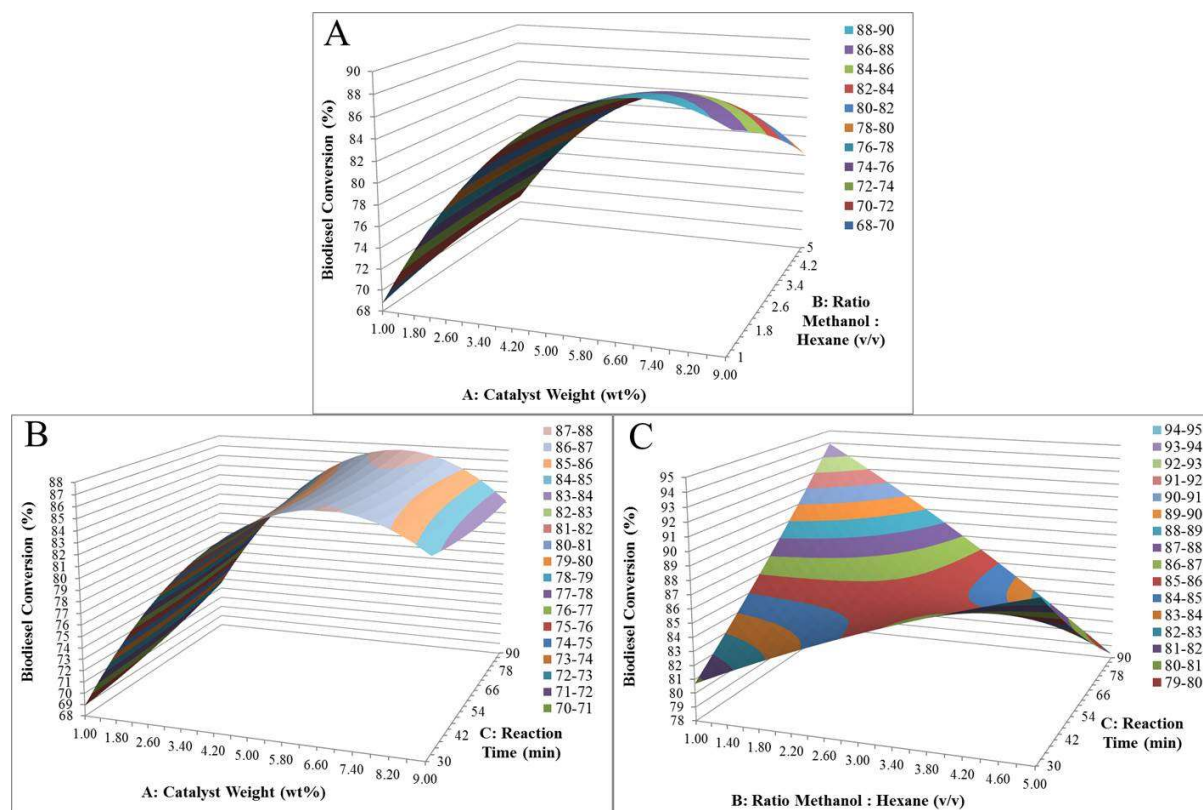


Fig-2: Response Surface Graphics of (A) Catalyst Weight and Ratio Methanol to Hexane; (B) Catalyst Weight and Reaction Time; and (C) Ratio Methanol to Hexane and Reaction Time on Biodiesel Conversion of the RES-intensified DT of wet SCG Biomass using BaO Catalyst.

CONCLUSION

The RES method combined with either CaO or BaO as heterogeneous catalyst provide a new approach in one-pot simultaneously extracting and converting lipid from wet SCG biomass. BaO showed better catalytic activity with biodiesel conversion three times higher than CaO. No significant effect of all parameters was detected either for CaO or BaO. The maximum biodiesel conversion of ~99% predicted based on quadratic equation model could be achieved in reaction condition of CaO weight of 23 wt.%, ratio methanol : hexane of 1:7.5 and reaction time of 150 mins which is beyond the level set up for parameters. Further, for BaO catalysed the DT of wet SCG biomass, the optimum biodiesel conversion of 90% could be accomplished in reaction condition of catalyst weight 6.5 wt.%, ratio methanol to hexane of 1:5 and reaction time of 30 mins. The RES-intensified the DT of wet SCG biomass using BaO as catalyst offer a simple and effective method as purification of biodiesel product could be done through different phase separation and evaporation of the co-solvent.

ACKNOWLEDGEMENT

The authors would like to thank the Ministry of Research and Technology/National Research and Innovation Agency - Indonesia and Universitas Sumatera Utara for research grant No. 11/E1/KP-PTNBH/2019 date 29th March 2019.

REFERENCES

1. E. K. Sitepu, K. Heimann, C. L. Raston, and W. Zhang, *Renewable and Sustainable Energy Reviews*, **123**, 109762(2020), <https://doi.org/10.1016/j.rser.2020.109762>
2. M. J. Haas, A. J. Mcaloon, W. C. Yee, and T. A. Foglia, *Bioresource Technology*, **97**, 671(2006), <http://dx.doi.org/10.1016/j.biortech.2005.03.039>

3. F. Harahap, S. Silveira, and D. Khatiwada, *Energy*, **170**, 62(2019), <https://doi.org/10.1016/j.energy.2018.12.115>
4. S. R. Dasari, A. J. Chaudhary, V. V. Goud, N. Sahoo, and V. N. Kulkarni, *Energy Conversion and Management*, **142**, 200(2017), <https://doi.org/10.1016/j.enconman.2017.03.044>
5. E. K. Sitepu, D. B. Jones, Y. Tang, S. C. Leterme, K. Heimann, W. Zhang, and C. L. Raston, *Chemical Communications*, **54**, 12085(2018), <http://dx.doi.org/10.1039/C8CC07610C>
6. S. Jazzar, P. Olivares-Carrillo, A. Pérez De Los Ríos, M. N. Marzouki, F. G. Acién-Fernández, J. M. Fernández-Sevilla, E. Molina-Grima, I. Smaali, and J. Quesada-Medina, *Applied Energy*, **148**, 210(2015), <http://dx.doi.org/10.1016/j.apenergy.2015.03.069>
7. S. X. Tan, S. Lim, H. C. Ong, and Y. L. Pang, *Fuel*, **235**, 886(2019), <https://doi.org/10.1016/j.fuel.2018.08.021>
8. S. K. Yellapu, R. Kaur, and R. D. Tyagi, *Bioresource Technology*, **224**, 365(2017), <http://dx.doi.org/10.1016/j.biortech.2016.11.037>
9. M. Barekati-Goudarzi, P. D. Muley, A. Clarens, D. B. Nde, and D. Boldor, *Biomass and Bioenergy*, **107**, 353(2017), <https://doi.org/10.1016/j.biombioe.2017.09.006>
10. S. Y. Chua, L. a. P. Periasamy, C. M. H. Goh, Y. H. Tan, N. M. Mubarak, J. Kansedo, M. Khalid, R. Walvekar, and E. C. Abdullah, *Journal of Industrial and Engineering Chemistry*, **81**, 41(2020), <https://doi.org/10.1016/j.jiec.2019.09.022>
11. H. H. Mardhiah, H. C. Ong, H. H. Masjuki, S. Lim, and H. V. Lee, *Renewable and Sustainable Energy Reviews*, **67**, 1225(2017), <https://doi.org/10.1016/j.rser.2016.09.036>
12. R. Olivia, N. Jamarun, S. Arif, and Y. A. Sirin, *Rasayan Journal of Chemistry*, **10**, 160(2017), <http://dx.doi.org/10.7324/RJC.2017.1011555>
13. Helmiyati, G. Abbas, Y. Budiman, and S. Ramadhani, *Rasayan Journal of Chemistry*, **13**, 298(2020), <http://dx.doi.org/10.31788/RJC.2020.1315497>
14. J. Nair, Y. Murthy, M. Ramesh, and G. Edeira, *Rasayan Journal of Chemistry*, **12**, 1757(2019), <http://dx.doi.org/10.31788/RJC.2019.1245273>
15. D. Y. C. Leung, X. Wu, and M. K. H. Leung, *Applied Energy*, **87**, 1083(2010), <http://dx.doi.org/10.1016/j.apenergy.2009.10.006>
16. O. S. Stamenković, Z. B. Todorović, and V. B. Veljković, *Chemical Engineering & Technology*, **37**, 2143(2014), <https://doi.org/10.1002/ceat.201300685>
17. D. M. Marinković, M. V. Stanković, A. V. Veličković, J. M. Avramović, M. R. Miladinović, O. O. Stamenković, V. B. Veljković, and D. M. Jovanović, *Renewable and Sustainable Energy Reviews*, **56**, 1387(2016), <https://doi.org/10.1016/j.rser.2015.12.007>
18. X. Liu, H. He, Y. Wang, S. Zhu, and X. Piao, *Fuel*, **87**, 216(2008), <http://dx.doi.org/10.1016/j.fuel.2007.04.013>
19. P. R. Pandit and M. H. Fulekar, *Journal of Environmental Management*, **198**, 319(2017), <https://doi.org/10.1016/j.jenvman.2017.04.100>
20. A. W. Go, S. Sutanto, L. K. Ong, P. L. Tran-Nguyen, S. Ismadji, and Y.-H. Ju, *Renewable and Sustainable Energy Reviews*, **60**, 284(2016), <http://dx.doi.org/10.1016/j.rser.2016.01.070>
21. F. Zhang, Z. Fang, and Y.-T. Wang, *Applied Energy*, **155**, 637(2015), <http://dx.doi.org/10.1016/j.apenergy.2015.06.044>
22. J. B. Tarigan, M. Ginting, S. N. Mubarakah, F. Sebayang, J. Karo-Karo, T. T. Nguyen, J. Ginting, and E. K. Sitepu, *RSC Advances*, **9**, 35109(2019), <https://doi.org/10.1039/C9RA08038D>
23. S. Wu, S. Deng, J. Zhu, M. A. Bashir, and F. Izuno, *Journal of Cleaner Production*, **228**, 405(2019), <https://doi.org/10.1016/j.jclepro.2019.04.311>
24. N. Tuntiwiwattanapun, E. Monono, D. Wiesenborn, and C. Tongcumpou, *Industrial Crops and Products*, **102**, 23(2017), <https://doi.org/10.1016/j.indcrop.2017.03.019>
25. N. Kondamudi, S. K. Mohapatra, and M. Misra, *Journal of Agricultural and Food Chemistry*, **56**, 11757(2008), <https://doi.org/10.1021/jf802487s>
26. J. Park, B. Kim, and J. W. Lee, *Bioresource Technology*, **221**, 55(2016), <https://doi.org/10.1016/j.biortech.2016.09.001>

27. S. Ezzah-Mahmudah, I. M. Lokman, M. I. Saiman, and Y. H. Taufiq-Yap, *Energy Conversion and Management*, **126**, 124-131(2016), <http://dx.doi.org/10.1016/j.enconman.2016.07.072>
28. V. Mahdavi and A. Monajemi, *Journal of the Taiwan Institute of Chemical Engineers*, **45**, 2286-2292(2014), <http://dx.doi.org/10.1016/j.jtice.2014.04.020>
29. N. Mansir, Y. H. Taufiq-Yap, U. Rashid, and I. M. Lokman, *Energy Conversion and Management*, **141**, 171-182(2017), <https://doi.org/10.1016/j.enconman.2016.07.037>
30. H. Amani, Z. Ahmad, and B. H. Hameed, *Applied Catalysis A: General*, **487**, 16-25(2014), <https://doi.org/10.1016/j.apcata.2014.08.038>
31. X. Yin, X. Duan, Q. You, C. Dai, Z. Tan, and X. Zhu, *Energy Conversion and Management*, **112**, 199-207(2016), <http://dx.doi.org/10.1016/j.enconman.2016.01.026>
32. B. Changmai, C. Vanlalveni, A. P. Ingle, R. Bhagat, and L. Rokhum, *RSC Advances*, **10**, 41625-41679(2020), <http://dx.doi.org/10.1039/D0RA07931F>
33. S. Nasreen, M. Nafees, L. A. Qureshi, M. S. Asad, A. Sadiq, and S. D. Ali, Review of Catalytic Transesterification Methods for Biodiesel Production, (Eds), Biofuels-State of Development, IntechOpen, **2018**: <https://doi.org/10.5772/intechopen.75534>
34. H. Mootabadi, B. Salamatnia, S. Bhatia, and A. Z. Abdullah, *Fuel*, **89**, 1818-1825(2010), <https://doi.org/10.1016/j.fuel.2009.12.023>

[RJC-6521/2021]