

Catalytic Cracking of Methyl Ester Derived from Used Cooking Oil Over Ni-Impregnated Activated Charcoal Catalyst

N. Nazarudin^{1,2,3,4*}, Y.Y. Hans^{2,3}, O. Alfernando^{2,3,4}, U. Ulyarti^{3,4,5}, I.B Adilina⁶

¹Department of Chemistry Education, Faculty of Faculty of Teacher Training and Education (FKIP), Universitas Jambi, Jambi, Indonesia

²Department of Chemical Engineering, Engineering Faculty, Universitas Jambi, Jambi, Indonesia

³Energy and Nano Material Centre, LPPM, Universitas Jambi, Jambi, Indonesia.

⁴Centre of Excellence on Bio-Geo Material and Energy

⁵Department of Agricultural Product of Technology, Universitas Jambi, Jambi, Indonesia

⁶Research Centre for Chemistry, National Research and Innovation Agency, Indonesia

*) Corresponding author: nazarudin@unja.ac.id

(Received: 29 January 2022; Published: 27 June 2022)

Abstract

The world's oil and gas reserve resources have been suffering from serious depletion along with their increasing demand by industries and transportations. It is estimated that Indonesia will suffer from a fuel crisis in the next few years. One way to solve this problem is by finding the alternative energy sources, especially those derived from renewable raw materials. This study was conducted to obtain alternative renewable energy sources through catalytic cracking of used cooking oil-derived methyl ester into biofuel using activated charcoal catalyst. The activated charcoal was made of oil palm shell and was further treated with nickel solutions of various concentrations (1%, 2%, 3%) to produce Ni-charcoal catalyst. This catalyst was then used for catalytic cracking of methyl esters derived from used cooking oil at various reaction temperature (400°C, 450°C and 500°C). The SEM-EDX analysis showed that nickel metal was successfully embedded into activated charcoal where the highest concentration of nickel (18.4%) was found at an impregnation treatment using 2% of nickel solution. The catalytic cracking of methyl esters derived from used cooking oil using Ni-charcoal catalyst impregnated with 3% nickel solution at 400°C produced the highest oil liquid fraction (OLF 65.58%) and the highest ratio of OLF/gas.

Keywords: charcoal; used cooking oil; catalytic cracking; impregnation, nickel

How to Cite This Article: Nazarudin, N., Ulyarti, U., Alfernando, O., & Hans, Y. Y. (2022). Catalytic Cracking of Methyl Ester from Used-Cooking Oil Using Ni-Impregnated Active Charcoal Catalyst. *Reaktor*, 22(1), 21-27. <https://doi.org/10.14710/reaktor.22.1.21-27>

INTRODUCTION

The depletion of fossil fuel resources has encouraged scientists around the world to look for new sources for fuel. A large number of researches have been carried out to develop fuels from renewable sources, especially the biodiesel. Biodiesel may be produced from many sources available in nature which each of them has

unique physicochemical characteristics (Su et al., 2019, Ahmad et al., 2019, Bussler et al., 2019, DeMarini et al., 2019, Kim et al., 2019). The sustainable supply of low-cost raw materials for biodiesel is very important as the production cost of biodiesel is mainly depend on its raw material (Kayode & Hart, 2017). Other potential sources for biodiesel are from household and biomass wastes

including used cooking oil (Moazeni et al., 2019). Used cooking oil is a more promising raw material for biodiesel compare to the fresh vegetable oils. Depending on the origin of cooking oil, biodiesel production from used cooking oil mostly employed transesterification process (Keera, et al., 2018, Goh et al., 2019, Kim, et al., 2019, Kouzu et al., 2020) and hydrocracking (Menshhein et al., 2019).

Biodiesels derived from transesterification process face some problems, especially due to their high freeze point which limits their application in countries with winter season (Kayode & Hart, 2017). Other limitation is the production of longer chain hydrocarbon compounds that may cause overmuch plugging at fuel filters of the diesel engine. One route for biodiesel quality improvement is by using cracking process of vegetable oil or its transesterified products either with catalyst (Sadrameli and Seifi, 2016) or without catalyst (Seames et al., 2010). The use of catalyst was found to produce lower acidity than those without catalyst leading to an improved biofuel quality (Romero et al., 2016, Sadrameli and Seifi, 2016). However, the catalysts used in the production of biofuels from vegetable oils and their derivative esters are mostly expensive. Hence, the use of palm shell waste as a raw material for catalyst production can be expected to reduce the cost for catalyst. Nevertheless, palm shell charcoal alone has been reported to have low productivity. An improvement step can be performed to obtain a higher catalyst productivity through the attachment of polyvalent metal, such as nickel, cobalt, molybdenum, chrom, etc. Impregnation method is the simplest way to attach Ni to activated charcoal catalyst. This research was carried out to fabricate Ni-charcoal catalyst and to study the catalytic cracking of used cooking oil-derived methyl ester for obtaining an alternative energy source through.

MATERIAL AND METHODS

Materials

Used cooking oil was obtained from the leftover of domestic activity and was obtained after 3 cycles of frying. The charcoal was produced from palm shell supplied by a Palm Oil company in Jambi, Indonesia. The chemicals, such as methanol, Nitrate nonahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$), sodium hydroxide, acetic acid were supplied from Merck (Germany), while nitrogen and hydrogen were supplied from Samator Indonesia Co. Ltd.

Methods

This research was carried out in three steps. First, the preparation of methyl ester from used cooking oil. Meanwhile, the second and third steps were catalyst preparation and catalytic cracking of the methyl ester obtained from the first step. The scheme of the procedure is shown in Figure 1.

Preparation of Methy Ester from Used Cooking Oil

The preparation of methyl ester from used cooking oil was carried out following the method

previously described by Alfernando et al. (2019). The used cooking oil was passed through an activated charcoal bed. A glass tube with 50 cm length and 2-inch diameter was filled with activated charcoal until half-filled and was further used as an adsorption unit. Then, approximately 600 mL of used cooking oil was filtered through this adsorption unit. The filtered oil was collected and ready for methyl ester synthesis.

The synthesis of methyl ester used a volume ratio of used cooking oil and ethanol of 1:3 and 0.25 wt.% sodium hydroxide solution as the catalyst. A predetermined weight of sodium hydroxide crystal was dissolved in methanol and then mixed with used cooking oil. This mixture was heated at 65°C with continuous stirring for one hour. Then, the resulting solution was distilled at 80°C . Methyl ester was separated from glycerol using a separating funnel. Methyl ester was collected and settled for 24 hours after which it was washed 3 times using distilled water at 50°C until no residual sodium hydroxide was identified and then heated at 100°C to remove the residual moisture. The volume and weight of methyl ester were recorded.

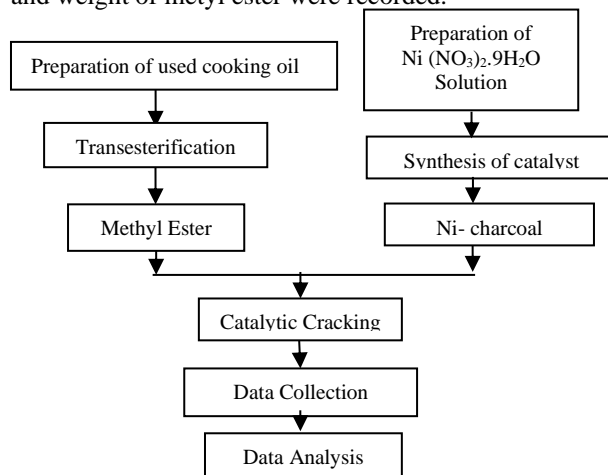


Figure 1. Schematic procedures of the research

Preparation of $\text{Ni}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ Solution

A carefully 44.1105 gram $\text{Ni}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ was weighed and placed in a 250 ml volumetric flask. The volume was filled using distilled water to produce a solution with 3% concentration. The 1% and 2% Ni solution were prepared by diluting the 3% Ni-solution.

Charcoal Activation

The activation of charcoal was carried out following the method presented by Prabasari *et al.* (2019). Charcoal from palm shell was activated using sodium hydroxide solution and followed by a neutralisation using acetic acid. solution. Charcoal, distilled water and sodium hydroxide with weight ratio 1: 3: 1 were stirred using magnetic stirrer for 2 hours at $\pm 40^\circ\text{C}$. The charcoal was separated from the liquid solution by filtration and washing. The charcoal was soaked in 5 mL acetic acid. solution 25% 30 min, filtered and washed using distilled water until pH of the washing solution was neutral. The activated charcoal was dried in oven dryer at 105°C for 4 hours.

The Synthesis of Ni-Charcoal Catalyst using Impregnation Method

Ni-charcoal catalysts were synthesized following method presented by Prabasari *et al.* (2019). The activated charcoal was introduced in 1%, 2% and 3% Ni-solution and was continuously stirred for 24 hours. The weigh ratio of charcoal to Ni-solution was 1: 10. The catalysts were recovered by filtration. The recovered catalysts were further calcined at 550°C. The catalysts are labelled as follow:

AC = active charcoal catalyst

AC-Ni-1 = Ni-charcoal catalyst produced using 1% Ni-solution

AC-Ni-2 = Ni-charcoal catalyst produced using 2% Ni-solution

AC-Ni-3 = Ni-charcoal catalyst produced using 3% Ni-solution

Catalytic Cracking of Methyl Ester

The catalytic cracking employed a catalyst to methyl ester mass ratio 1:30. The reactor was heated to the desirable temperature (400°C, 450°C, 500°C). Methyl ester was injected into the horizontal reactor and nitrogen gas valve was opened to deliver the gas through the reactor. The heated methyl ester flowed to vertical reactor and finally the catalytic cracking products flowed to an ice trap to condense the product. The overall reaction took place for 100 minutes. The oil product was brownish yellow in color. The schematic diagram of the catalytic reactor was the same as previously reported (Prabasari *et al.*, 2019).

Catalyst and Cracking Products Characterisation

The catalyst was characterised using XRD dan SEM-EDX at Sepuluh November Institute of Technology. The liquid cracking product was analysed for its density in Laboratory of Energy at Energy and Nanomaterial Study Centre, LPPM University of Jambi. Analyses of calorific content was carried out at Pertamina Laboratory. Gravimetric analysis was used to determine yields of each cracking products and percent residu using equations following (Nazarudin, 2012).

$$\text{Yields of CP} = \left(\frac{\text{weigh of CP}}{\text{initial weigh of feed}} \right) \times 100 \% \quad (1)$$

Where CP = Cracking product that can be either liquid or gas

$$\% \text{ residu} = \left(\frac{\text{weigh of residu}}{\text{initial weigh of feed}} \right) \times 100 \% \quad (2)$$

RESULTS AND DISCUSSION

Catalyst Characterization

Based on their XRD patterns shown in Figure 2, the activated charcoal-based catalysts shown to have high intensity 2θ at 21.8°; 21.9°; 26.5°; 36.2°; 42.2°. The similar XRD patterns among these catalysts showed that the impregnation procedures did not significantly affect the alteration of structural phases or crystallinity in the catalyst. The XRD pattern confirm that the catalysts

were amorphous as also confirmed by its SEM-EDX image (Figure 3). Upon scanning using 1000× magnification, it was shown that the activated charcoal has aggregates pores of nanometer size and predicted to have nano scale. The SEM-EDX analysis also showed that the activated charcoal contained silica, carbon, phosphor and calcium (Table 1). Being the major element of the active charcoal, the carbon structure was further used as Ni support in the catalyst. As shown in Figures 4 and Table 2, Ni was succesfully impregnated to activated charcoal, being impregnation using 2% Ni solution produced the highest Ni content in the Ni-charcoal catalyst.

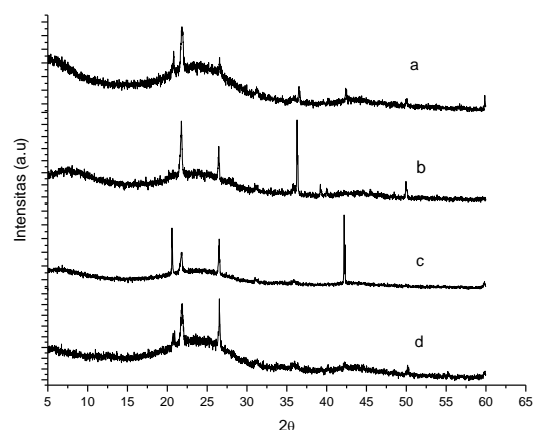


Figure 2. XRD Diffractograms of the Catalyst (a) Active Charcoal (b) AC-Ni-1 (c) AC-Ni-2 (d) AC-Ni-3

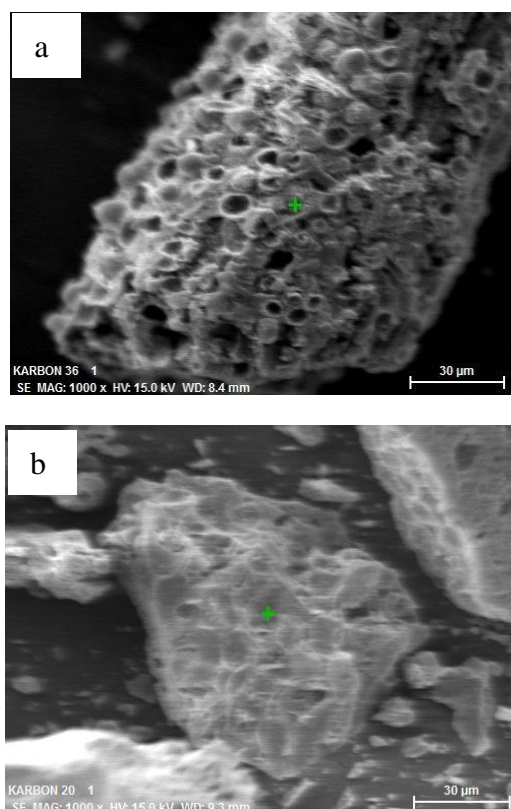


Figure 3. SEM Images of Activated Charcoal Catalyst (a) and AC-Ni-2 (b)

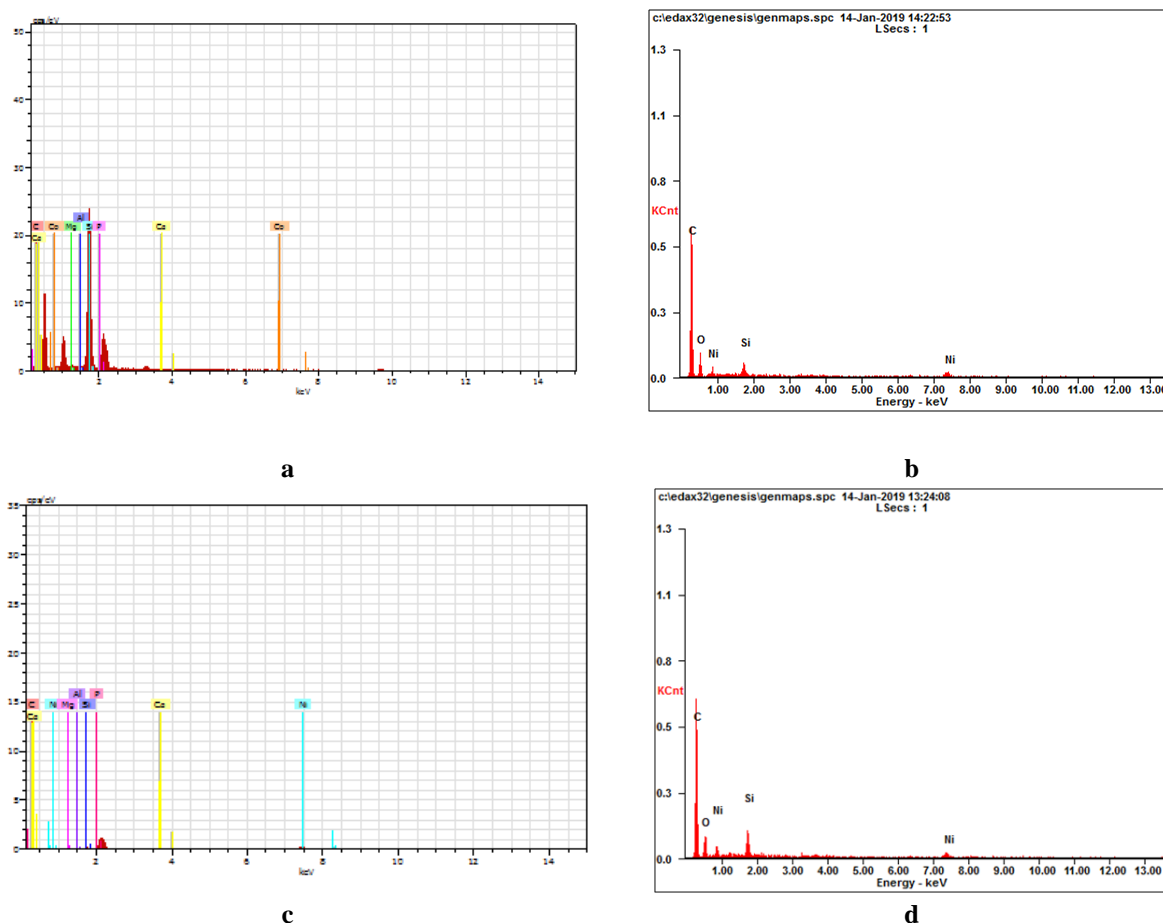


Figure 4. EDX Spectra for Active Charcoal (a), AC-Ni-1 (b), AC-Ni-2 (c), AC-Ni-3 (d)

Table 1. The Composition of active charcoal

Number	Element	Composition (wt.%)
1.	Si	35.35
2.	C	62.32
3.	P	2.14
4.	Ca	0.20

Table 2. Composition of active charcoal-based catalyst revealed by SEM-EDX

No	Sample	Composition (wt.%)				Ratio C/Ni
		Si	C	O	Ni	
1.	AC-Ni-1	8.02	62.16	23.09	8.23	7.55
2.	AC-Ni-2	8.02	59.15	0.00	18.42	3.21
3.	AC-Ni-3	4.18	64.16	22.44	9.23	6.95

Products of Catalytic Cracking

The cracking products of used cooking oil-derived methyl ester using activated charcoal and Ni-active charcoal produced were oil liquid (33.34% - 65.58%) and followed by gas (22.50% - 66.66%). The detail products are presented in Table 3. The impregnation of active charcoal into Ni salt solution showed to increase the performance of the Ni-active charcoal catalyst. The highest oil liquid fraction to gas ratio was obtained at 450° C using AC-Ni-2. However, at this operating condition resulted in a large amount of residue because less methyl ester feed underwent carbon chain breakage, but imperfect combustion instead. Although the Ni content of AC-Ni-2 is the highest among the catalysts produced in this study, it did not perform catalytic cracking performance as expected. The more preferred condition for used cooking oil-derived methyl ester was using AC-Ni-3 which produced the highest liquid oil fraction and low residue. This overall results showed that the use of different temperatures and Ni content in the catalyst determined product selectivity (Figure 5).

Table 3. The Profile of Products of Catalytic Cracking of used Cooking Oil-Originated Methyl Ester over Activated Charcoal and Ni-activated Charcoal Catalysts

Catalyst	Methyl Ester (g)	Temperature (°C)	Liquid Yield (%)	Residue (%)	Gas Yield (%)
AC-Ni-3	31.12	400	65.58	4.24	30.17
	32.12	450	38.85	30.79	30.35
	31.04	500	57.54	2.58	39.88
AC-Ni-2	32.51	400	59.09	3.08	37.83
	29.56	450	58.76	18.74	22.50
	25.88	500	33.38	2.13	64.49
AC-Ni-1	32.60	400	58.62	1.07	40.31
	31.10	450	33.34	0.00	66.66
	31.37	500	63.66	1.53	34.81
AC	29.65	400	43.74	4.59	51.67
	31.54	450	62.43	1.30	36.27
	31.16	500	52.31	1.06	46.63

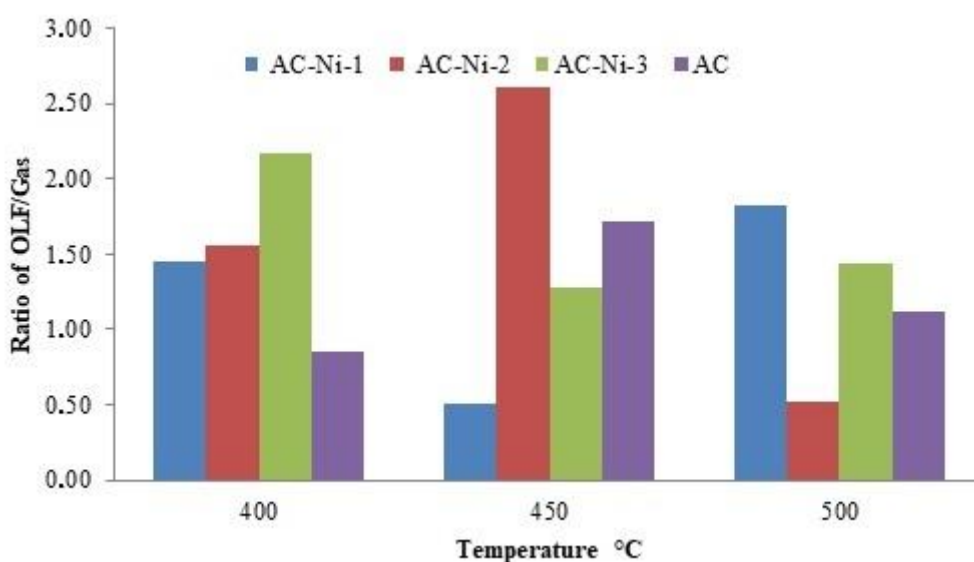


Figure 5. Ratio Oil Liquid Fraction (OLF)/Gas Produced by Catalytic Cracking of used Cooking Oil-Originated Methyl Ester using Activated Charcoal (AC) and AC Impregnated by Various Concentration of Ni Solutions

Characterization of Oil Liquid Fraction (OLF) from Catalytic Cracking

The OLF produced from catalytic cracking of used cooking oil-derived methyl ester had not a distinct densities (Table 4). However, the density of these liquid fractions was lower than the density of their raw material (density of used cooking oil was 0.9534 g/cm³ and that of methyl ester was 0.9154 g/cm³). Cracking process breaks double bonds and evaporates some carbon compound leading to lower density of the product. However, the densities of OLFs were still slightly higher than the density of B20 (0.88 g/cm³) which composed of 20% methyl ester and 80% commercial petroleum diesel

produced by PT. Pertamina (an Indonesian owned refinery industry). The methyl ester contained 49.12% C19 compounds and 32.44% C17 compound as showed by GCMS analysis (Alferando et al., 2019). Catalytic cracking of the methyl ester changed the composition to 47.55% C17 carbon compound and 40.35% C17/C19 carbon compound (Table 5). Furthermore, the calorific value of the highest percentage of OLF produced from catalytic cracking of used cooking oil-derived methyl ester using AC-Ni-3 catalyst at 400 °C was found to be higher than that of methyl ester and B20 (Table 6.)

Table 4. Density of OLF from catalytic cracking of used cooking oil-derived methyl ester using several Ni-charcoal catalysts

No.	Temperature (°C)	Catalyst	Density (g/cm ³)
1	400	AC-Ni-1	0.9118
2	450	AC-Ni-1	0.9134
3	500	AC-Ni-1	0.9059
4	400	AC-Ni-2	0.9086
5	450	AC-Ni-2	0.9019
6	500	AC-Ni-2	0.9130
7	400	AC-Ni-3	0.9156
8	450	AC-Ni-3	-
9	500	AC-Ni-3	0.912

Table 5. GCMS Analysis of OLF from catalytic cracking of used cooking oil-derived methyl ester using AC-Ni-3 catalyst

No	RT	%Area	Similarity Index	Compound	Molecular Formula	Molecular weight (g/mol)
1.	30.10	3.59	91	<i>Dodecanoic acid, methyl ester</i>	C ₁₃ H ₂₆ O ₂	214
				<i>Pentadecanoic acid, 14-methyl-, methyl ester</i>	C ₁₇ H ₃₄ O ₂	270
2.	34.99	2.15	88	<i>Decanoic acid, methyl ester</i>	C ₁₁ H ₂₂ O ₂	186
				<i>9-Hexadecenoic acid, methyl ester</i>	C ₁₇ H ₃₂ O ₂	268
3.	38.97	0.60	84	<i>Pentadecanoic acid, 14-methyl-, methyl ester</i>	C ₁₇ H ₃₄ O ₂	270
4.	39.48	47.55	91	<i>9,12-Octadecadienoic acid, methyl ester, (E, E)-</i>	C ₁₉ H ₃₄ O ₂	294
5.	42.84	3.16	86	<i>11-Octadecenoic acid, methyl ester</i>	C ₁₉ H ₃₆ O ₂	296
				<i>9-Hexadecenoic acid, methyl ester, (Z)-</i>	C ₁₇ H ₃₂ O ₂	268
6.	43.02	40.35	90	<i>Pentadecanoic acid, 14-methyl-, methyl ester</i>	C ₁₇ H ₃₄ O ₂	270

Table 6. Calor content of methyl ester, biodiesel and oil liquid fraction produced from catalytic cracking of methyl ester

No	Samples	Calorific content (cal/g)
1	Metil Ester	9,237.3671
2	Biodiesel (B20)	9,381.8221
3	Oil Liquid fraction (AC-Ni-3)	10,088.800

CONCLUSION

Impregnation of activated charcoal using 2% Ni (NO₃)₂·9H₂O solution produced charcoal catalyst with the highest nickel content (18.42%). Catalytic cracking of used cooking oil-based methyl ester using Ni-impregnated activated charcoal catalyst showed that the ideal condition for liquid fraction production was

cracking using Ni-impregnated catalyst in 3% Ni (NO₃)₂·9H₂O at 400°C. At this condition, the cracking of methyl ester produced 65.58% OLF with calorific content higher than the commercial Biodiesel (B20).

REFERENCES

Ahmad, T., Danish, M., Kale, P., Geremew, B., Adeloju, S.B., Nizami, M., Ayoub, M., (2019). Optimization of process variables for biodiesel production by transesterification of flaxseed oil and produced biodiesel characterizations. *Renew. Energy* 139, 1272–1280. <https://doi.org/10.1016/j.renene.2019.03.036>

Alfernando, O., Sarip, R., Anggraini, T., Nazarudin, N., (2019). Catalytic Cracking of Methyl Ester from Used Cooking Oil with Ni-Ion-Exchanged ZSM-5 Catalyst.

- Makara J. Sci. 23, 169–178.
<https://doi.org/10.7454/mss.v23i4.11509>
- Bussler, L., Izida, T., Lima, S.M., Andrade, L.H.C., (2019). Comparison of optical spectroscopy techniques for monitoring the stages of thermoxidation of soybean biodiesel. *Spectrochim. Acta - Part A Mol. Biomol. Spectrosc.* 217, 190–196.
<https://doi.org/10.1016/j.saa.2019.03.040>
- DeMarini, D.M., Mutlu, E., Warren, S.H., King, C., Gilmour, M.I., Linak, W.P., (2019). Mutagenicity emission factors of canola oil and waste vegetable oil biodiesel: Comparison to soy biodiesel. *Mutat. Res. - Genet. Toxicol. Environ. Mutagen.* 846, 403057.
<https://doi.org/10.1016/j.mrgentox.2019.05.013>
- Goh, B.H.H., Ong, H.C., Cheah, M.Y., Chen, W.H., Yu, K.L., Mahlia, T.M.I., (2019). Sustainability of direct biodiesel synthesis from microalgae biomass: A critical review. *Renew. Sustain. Energy Rev.* 107, 59–74.
<https://doi.org/10.1016/j.rser.2019.02.012>
- Kayode, B., Hart, A., (2017). An overview of transesterification methods for producing biodiesels from waste cooking oil. *Biofuels.*
<https://doi.org/10.1080/17597269.2017.1306683>
- Keera, S.T., El Sabagh, S.M., Taman, A.R., (2018). Castor oil biodiesel production and optimization. *Egypt. J. Pet.* 27, 979–984.
<https://doi.org/10.1016/j.ejpe.2018.02.007>
- Kim, G.Y., Seo, Y.H., Kim, I., Han, J.I., (2019). Co-production of biodiesel and alginate from *Laminaria japonica*. *Sci. Total Environ.* 673, 750–755.
<https://doi.org/10.1016/j.scitotenv.2019.04.049>
- Kouzu, M., Kuwako, T., Ohto, Y., Suzuki, K., Kojima, M., (2020). Single stage upgrading with the help of bifunctional catalyst of Pt supported on solid acid for converting product oil of triglyceride thermal cracking into drop-in fuel. *Fuel Processing Technology* 202, 2-7.
<https://doi.org/10.1016/j.fuproc.2020.106364>
- Mensshhein, G., Costa, V., Chiarello, L.M., Scharf, D.R., Simianato, E.L., Botton, V., Meier, H.F., Wiggers, V.R., Ender, L., (2019). Concentration of renewable products of crude bio-oil from thermal cracking of methyl ester in castor oil. *Renewable Energy* 142, 561-568.
<https://doi.org/10.1016/j.renene.2019.04.136>
- Moazeni, F., Chen, Y.C., Zhang, G., (2019). Enzymatic transesterification for biodiesel production from used cooking oil, a review. *J. Clean. Prod.* 216, 117–128.
<https://doi.org/10.1016/j.jclepro.2019.01.181>
- Nazarudin (2012). Catalytic Cracking of Plastic Waste Using Nanoporous Materials. *PhD Thesis*, University College London.
- Prabasari, I.G., Sarip, R., Rahmayani, S., Nazarudin, (2019). Catalytic Cracking of Used Cooking Oil Using Cobalt-impregnated Carbon Catalysts. *Makara J. Sci.* 23.
<https://doi.org/10.7454/mss.v23i3.11264>
- Romero, M.J.A., Pizzi, A., Toscano, G., Busca, G., Bosio, B., Arato, E., (2016). Deoxygenation of waste cooking oil and non-edible oil for the production of liquid hydrocarbon biofuels. *Waste Manag.* 47, 62–68.
<https://doi.org/10.1016/j.wasman.2015.03.033>
- Sadrameli, S.M., Seifi, H., (2016). Improvement of renewable transportation fuel properties by deoxygenation process using thermal and catalytic cracking of triglycerides and their methyl esters. *Appl. Therm. Eng.* 100, 1102–1110.
<https://doi.org/10.1016/j.applthermaleng.2016.02.022>
- Seames, W., Luo, Y., Ahmed, I., Aulich, T., Kubátová, A., Št'ávoová, J., Kozliak, E., (2010). The thermal cracking of canola and soybean methyl esters: Improvement of cold flow properties. *Biomass and Bioenergy* 34, 939–946.
<https://doi.org/10.1016/j.biombioe.2010.02.001>