Malaysian Journal of Catalysis 9 (2025) 31-35

Malaysian Journal of Catalysis
http://mjcat.utm.my/
MJCat
Research Article

Preparation of Mesoporous Al-MCM-41 and Its Application for Hydrocracking *Cerbera manghas* Oil

Desy Anggraini[1], Lenny Marlinda[1], Rahmi[1], Sudibyo[2], Muhammad Amin[2], Erik Prasetyo[2], Sugeng Priyanto[3], Abdul Aziz[4], Reva Edra Nugraha[5], Sun Theo Constan Lotebulo Ndruru[6], Dicky Annas[6], Indri Yati[6], Muhammad Nur Khoiru Wihadi[6], Aishah Abdul Jalil[7,8], Muhammad Al Muttaqii[6]*

[1]*Department of Chemistry, Faculty of Science and Technology, Jambi University, Jambi*
[2]*Research Center for Mining Technology, National Research and Innovation Agency (BRIN-Indonesia), South Lampung 35361, Indonesia*
[3]*Department of Mechanical Engineering, State University of Jakarta, East Jakarta 13220, Indonesia*
[4]*Department of Chemistry, Faculty of Science and Data Analytics, Institut Teknologi Sepuluh Nopember, Keputih, Sukolilo, Surabaya 60111, Indonesia*
[5]*Department of Chemical Engineering, Faculty of Engineering, Universitas Pembangunan Nasional "Veteran" Jawa Timur, Surabaya, East Java, 60294, Indonesia*
[6]*Research Center for Chemistry, National Research and Innovation Agency (BRIN), South Tangerang 15310, Indonesia*
[7]*Centre of Hydrogen Energy, Institute of Future Energy, Johor Bahru, Johor 81310 UTM, Malaysia*
[8]*Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, Johor Bahru, Johor 81310 UTM, Malaysia*

**Corresponding Author: almuttaqiimuhammad@gmail.com; muhammad.al.muttaqii@brin.go.id*

Article history:
Received 8 January 2025
Accepted 28 February 2025

ABSTRACT

Mesoporous Al-MCM-41 was successfully prepared by hydrothermal method over CTABr template. The catalyst was varied of stirring time during the synthesis process, with 4 and 8 h. The results obtained showed that Al-MCM-41 with 4 h stirring had a surface area of 184.8508 m^2/g and an 8 h stirring of 655.4759 m^2/g. The Al-MCM-41 was used as a catalyst for hydrocracking *cerbera manghas* oil. Based on GC-MS analysis, the products contain 1-methyl-indan ($C_{10}H_{12}$), cyclotetracosane ($C_{24}H_{28}$) when using Al-MCM-41 4h. Meanwhile, when using Al-MCM-41 8h catalysts, the products contain 1,3 tetradecadiene ($C_{14}H_{26}$), and 1-tetracosene ($C_{24}H_{28}$). All products still contain high oxygenate compounds. The presence of carboxylic acids indicates that the hydrogenation reaction has required high temperature to convert them into biofuel. The results demonstrated that the synthesized Al-MCM-41 had potential applications as catalyst in the hydrocracking of non-edible oil to produce biofuel.

Keywords: mesoporous Al-MCM-41, hydrocracking, *cerbera manghas* oil

| eISSN 0128-2581 |

1. INTRODUCTION

As global energy demand increases, reliance on fossil fuels has led to an energy crisis and significant environmental impacts. The burning of fossil fuels contributes greatly to greenhouse gas emissions, which are a major cause of global warming and climate change. Therefore, there is an urgent need to find alternative energy sources that are cleaner and more sustainable [1]. One of the alternative energy sources is biofuel. Biofuel is an alternative renewable energy source that is environmentally friendly and sustainable. By using biofuels, dependence on petroleum and other fossil fuels can be reduced. one of the promising sources of biofuel is non-edible oil because it is not related to the food supply chain like edible oil. there are many examples of non-edible oil that have potential such as agricultural waste, plantations and other plants [2–4]. One of the sources of raw materials for biofuel production is *cerbera manghas* oil [5,6]. *Cerbera manghas* trees grow abundantly in Indonesia, especially on the islands of Java and Sumatra. *Cerbera manghas* seeds produce 46-64% oil after being pressed [7].

Biofuel production can be carried out through the hydrocracking process. Hydrocracking is a cracking process by reacting oil with a certain amount of hydrogen gas at a certain temperature and pressure. The product of the hydrocracking method will produce biofuels in the form of straight chain liquid alkanes from C-15 to C-18 [8]. The hydrocracking process uses acidic catalysts such as zeolite, Al_2O_3, SiO_2, alumina silica, Al-MCM-41 and is embedded with transition metals such as Co, Mo, Ni, Cr, Zn, Pt [9]. The use of metals to increase the active site and increase the acidity of the catalyst, so that the catalyst can be more active and selective [10].

Al-MCM-41 is one of the promising catalysts. This is because Al-MCM-41 has pores with a mesopore size range (2-50 nm). The presence of mesopores can reduce gas products and increase liquid products [11,12]. Al-MCM-41 catalyst can be synthesized using hydrothermal technique using sodium aluminate, tetraethyl orthosilicate and cetyltrimethylammonium bromide materials which are stirred until homogeneous using a magnetic stirrer at room temperature for 5 days, then heated at 110°C for 6 h to evaporate the solution. Furthermore, the solid was calcined at 550°C with nitrogen flow for 1 h and air for 6 h. The diffractogram of Al-MCM-41 synthesis catalyst using X-Ray Diffraction showed a peak at $2\theta = 26.3°$ with the results of biodiesel production from nyamplung oil to free acid methyl ester showed a conversion efficiency of 98.15% [13]. Hydrocracking reactions using Al-MCM-41 and Pd/Al-MCM-41 catalysts produce different product components in the hydrocracking of FAME. Hydrocarbon production will increase if alcohol production tends to decrease when there is palladium impregnation treatment on mesoporous aluminosilicate catalysts [13].

In addition, Chen et al. [14] have reported the synthesis of mesoporous silica material (Al-MCM-41) from natural pearlite mineral without the addition of silica or aluminum reagents. The stirring process was carried out for 2 h. The surface area of Al-MCM-41 produced was 1024 m^2/g. Gonzales et al., [15] also reported the synthesis of Al-MCM-41 using different Si/Al ratios. The stirring process was carried out for 1 hour and the AlM41S-25 sample produced a large surface area of 1126 m^2/g.

The purpose of this study is to synthesize Al-MCM-41 catalyst from rice husk waste material as a source of silica, stirring time of the synthesized catalysts, and can be used as a catalyst for hydrocracking of *cerbera manghas oil*.

2. EXPERIMENTS

2.1 Materials

The materials used were sodium hydroxide (NaOH, Merck, ≥99%), sulfuric acid (H_2SO_4, Merck, 95-97%), hexadecyltrimethylammonium bromide (CTABr, Merck, ≥99%), aluminum oxide (γ-Al_2O_3, Merck, surface area 120-190 m^2/g), SiO_2 source from rice husk waste from local market. *Cerbera manghas* seed oil collected and pressed in the area of Jambi University, Jambi.

2.2. Methods

The silica used was made from rice husk waste using a modified procedure carried out by Battegazzero et al. (2014) [16]. The stages are rice husk added with 200 ml of H_2O and 20 ml (1.828M) of H_2SO_4, then stirred using a magnetic stirrer for 5 h at 70°C, filtered and dried for 12 h at 50°C. Then, it was calcined with air for 5 h at 600°C. The results were analyzed by X-ray fluorescence (XRF) to investigate the chemical composition and the elements contained especially the SiO_2 content. Mesoporous aluminosilicate synthesis using a modified procedure carried out by Nugraha et al. (2021) [17]. The phases involve dissolving 0.025 mol Na_2O in 5 mol H_2O, adding 0.25 mol SiO_2, 0.005 mol γ-Al_2O_3, and a 0.05 mol CTABr template, and stirring for 4 h at 40°C. The mixture was aged overnight at room temperature, and the hydrothermal method was carried out at 160 °C for 48 h. The result was then washed with distilled water to pH=7, dried overnight at 120°C, and finally calcined with air for 5 h at 550°C. The same technique was used for the synthesis mixture, with an 8-h stirring duration. All Samples were noted as Al-MCM-41 4 h and Al-MCM-41 8 h.

2.3 Hydrocracking Process

The hydrocracking procedure was carried out in a batch reactor containing 0.5 g of catalyst and coated with a heating element. Then 50 mL of *cerbera manghas* oil was added to the batch reactor. Flow H_2 until the reactor pressure reaches 30 bar, then close the H_2 valve and heat the reactor from room temperature to the desired operating temperature of 330°C, maintaining it for 2 h. The product was collected and analyzed using a Gas Chromatography Mass Spectrophotometer (GCMS) with Agilent brand, type 19091S-433:93.92873 HP-5MS 5% Phenyl Methyl Silox to identify the compounds contained.

3. RESULTS AND DISCUSSION

The extracted silica was analyzed using XRF to determine the chemical composition. The XRF characterization results are shown in Table 1. Table 1 shows that the highest content contained in the extracted rice husk is SiO_2 with a percentage of 95.6527% and Al_2O_3 of 1.6143%. Based on several previous studies, it was stated that RHA contains >90% silica [18,19]. According to Ismail et al. (2015) [20], the crystal structure for amorphous SiO_2 will form with high temperature combustion above 600 °C, while the SiO_2 crystalline phase begins to form above 900 °C and at 1100 °C crystalline SiO_2 crystals are formed with high intensity so that the amount of silica obtained decreases.

Table 1. XRF Results of Rice Husk Extraction

Compounds	% wt
MgO	1.297
Al_2O_3	1.614
SiO_2	95.653
P_2O_5	0.588
SO_3	0.230
K_2O	0.115
CaO	0.132
TiO_2	0.007
MnO	0.021
Fe_2O_3	0.248

The XRD analysis was performed to identify the phase and crystallinity of the mesoporous aluminosilicate synthesis catalyst. The diffractogram patterns were observed at 2θ in the range of 10-80°. The diffractogram of Al-MCM-41 with 4 h and 8 h of stirring time synthesis is shown in Fig. 1. The diffractogram of the catalyst shows a broadened peak at 2θ = 22-23°. This peak suggested that Al-MCM-41 catalyst has an amorphous phase [21,22]. These results are in accordance with the previous study which also produced a broadened peak at 2θ = 22-23° [12].

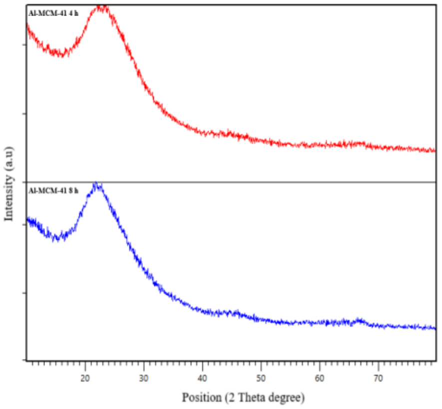

Fig. 1. The Diffractogram of Al-MCM-41 with 4 and 8 h of stirring time

The process of analyzing mesoporous materials can be known through Langmuir isotherm graphs based on the ratio of P/Po (mmHg) to the volume of N_2 per gram of sample (cm^3/g). The Langmuir isotherm graph shown in Fig. 2 illustrates a type IV graph which is a mesoporous material where there is a hysteresis loop in all different sample variations. A sharp gas change occurs at a relative pressure (P/Po) of about 0.1-0.3 which indicates the occurrence of mesoporous filling. All samples show the same pattern, in other words all samples indicate the presence of mesopores. This indication is reinforced by the occurrence of hysteresis or branching loops observed at relative pressure (P/Po) 0.3-0.9 in all samples [23]. In Fig. 2B, it can be seen that the pore diameter ranges from about 2-5 nm which is the pore size that can be used to access reactants. This indicates that the pore size distribution of all samples is in the mesoporous region (2-50 nm) [24].

Table 2 shows the physical properties of Al-MCM-41 stirred for 4 and 8 h. Al-MCM-41 with 8 h stirring time produces a larger surface area of 655.4759 m^2/g while Al-MCM-41 with 4 h stirring time produces a smaller surface area of 184.8508 m^2/g. This shows that the longer the stirring time process takes place, the greater the surface area produced. Table 2 shows that the surface area is influenced by pore volume and pore diameter, this is because the small pore diameter size will make the number of pores more and more so that the surface area will also be larger. In contrast to the pore volume, the larger the pore volume produced, the greater the surface area [25].

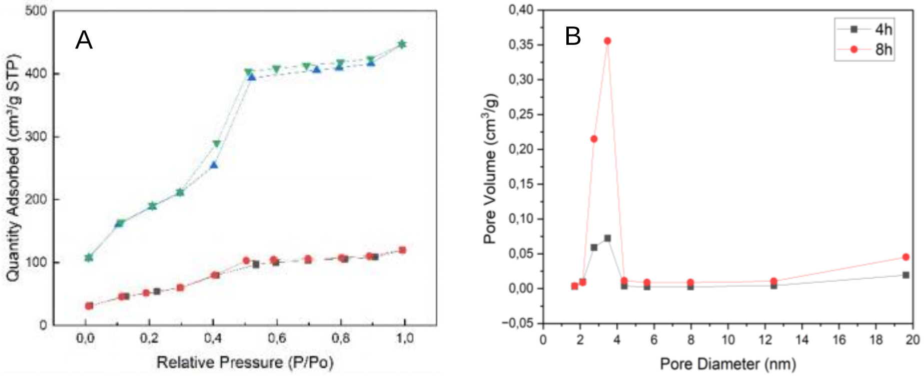

Fig. 2. (A) Comparison of Adsorption-Desorption of 4 h (red line) and 8 h Catalysts (green line), and (B) Pore Distribution Analysis of Catalyst by BJH Method

Table 2. Surface properties of Al-MCM-41

Samples	S_{area} (m^2/g)	S_{mikro} (m^2/g)	S_{meso} (m^2/g)	V_{tot} (cm^3/g)	V_{mikro} (cm^3/g)	V_{meso} (cm^3/g)
Al-MCM-41 4 h	184.851	2.764	182.086	0.186	0.001	0.185
Al-MCM-41 8 h	655.476	43.920	611.556	0.691	0.021	0.670

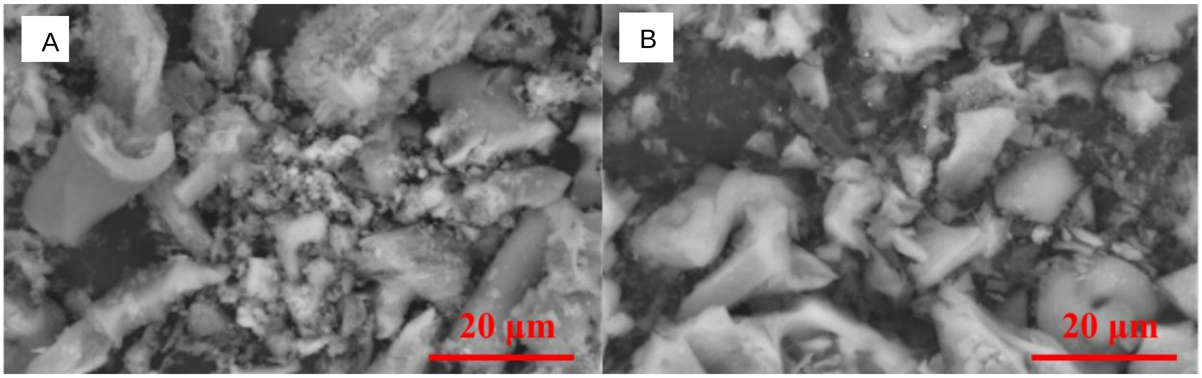

Fig. 3. 5000x SEM magnification (A) Al-MCM-41 4 h, and (B) Al-MCM-41 8 h

Fig. 3 shows the surface morphology of different catalysts using the SEM with magnification of 5000x. The non-uniformity of the visible particle size causes low crystallinity in the sample. This agglomeration and non-uniformity is supported by the research of Castro et al., (2021) [26], that the surface of Al-MCM-41 agglomerates in several particles with a non-uniform shape where some of them are round like a sleeve.

3.1 Catalytic Activity

The catalytic activity of Al-MCM-41 catalyst was tested in the hydrocracking process of *cerbera manghas* oil. The hydrocracking reaction was carried out for 2 h at temperature of 330 ºC. The GC-MS analyzed was utilized to obtained the qualitative and quantitative product for the catalytic activity test. Table 3 shown the composition of hydrocarbon. Based on GCMS analysis, biofuel hydrocarbons contain hydrocarbons and oxygenate compounds [27]. Fig. 4 shown the Gas chromatography-mass spectrometry spectra of biofuel at temperature of 330 ºC under pressure 30 bar in the batch reactor over (a) Al-MCM-41 4 h, and (b) Al-MCM-41 8 h catalyst with retention time of 22–24 min for different compounds of products. When using Al-MCM-41 4h catalyst, the products contain 1-methyl-indan ($C_{10}H_{12}$), cyclotetracosane ($C_{24}H_{28}$), and oxygenate compounds such as oleic acid, palmitic acid, and etc. Meanwhile, when using Al-MCM-41 8h catalysts, the products contain 1,3 tetradecadiene ($C_{14}H_{26}$), 1-tetracosene ($C_{24}H_{28}$), and still contain high oxygenate compounds. The presence of compounds that still contain a lot of oxygen such as carboxylic acids indicates that the hydrogenation reaction has not taken place properly at 330°C for 2 h to convert them into biofuel.

The oxygen removal process requires appropriate operating conditions of temperature, catalyst and reaction duration to optimize the decarboxylation/decarbonylation (HDC) and hydrodeoxygenation (HDO) reaction routes. The large amount of carboxylic acid shows that the hydrodeoxygenation reaction has not taken place well at 330°C with a reaction time of 2 h. An increase in temperature is needed to increase cracking activity and break large hydrocarbon chain molecules into small hydrocarbon chain molecules [28].

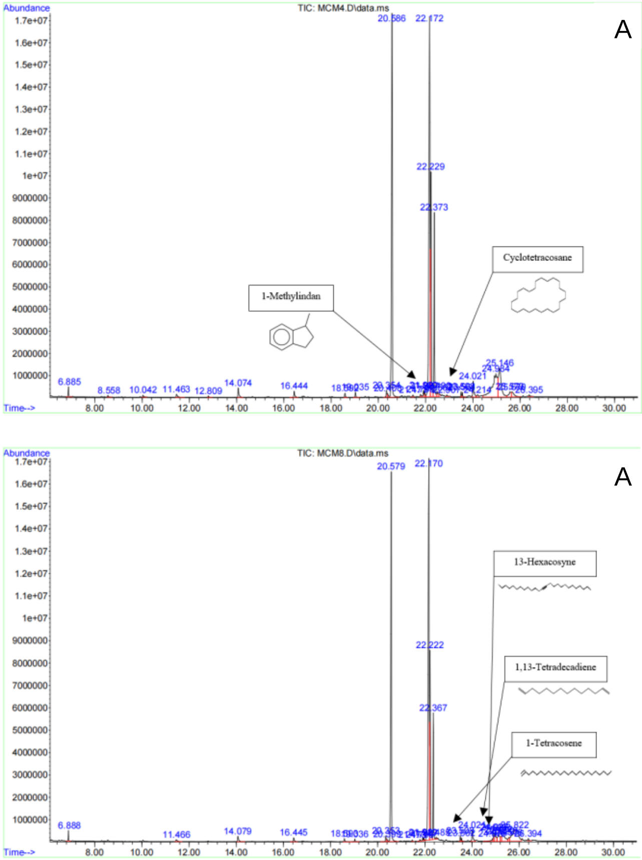

Fig. 4. Gas chromatography-mass spectrometry spectra of biofuel at temperature of 330 ºC under pressure 30 bar in the batch reactor over (A) Al-MCM-41 4 h, and (B) Al-MCM-41 8 h catalyst

The difference in biofuel products produced from Al-MCM-41 8-h and 4-h catalysts is due to the catalyst's properties, such as pore structure, surface area, and pore diameter. Al-MCM-41 synthesized for 8 hours has a more regular mesoporous structure with a larger pore volume and surface area than Al-MCM-41 synthesized for 4 hours. This can improve the accessibility of reactants and catalytic performance.

Table 3. The composition of hydrocarbon

Sample	**Composition of hydrocarbon**		
	C_{10}-C_{14}	**C_{15}-C_{22}**	**>C_{22}**
Al-MCM-41 4h	0.3	-	0.44
Al-MCM-41 8 h	0.8	-	1.48

4. CONCLUSION

Aluminosilicate synthesis catalyst has been successfully synthesized using materials made from rice husk waste with the addition of gamma alumina and CTABr template. The characteristics of aluminosilicate synthesis catalyst based on XRD analysis have amorphous phase at angle 2 theta = 22-23°. Based on GC-MS analysis, the product in the range fraction of biokerosene (C10-C14). The product of biofuel still contains high oxygenated compounds, it indicates that the hydrogenation reaction has not taken place properly at 330°C for 2 h to convert them into biofuel products.

ACKNOWLEDGEMENTS

This study was funded by the Research Organization for Nanotechnology and Materials – National Research and Innovation Agency (BRIN) research grant 2022 (No. 7/III/HK/2022). The authors would also like to thank Advanced Characterization Laboratories Serpong, National Research and Innovation Agency (BRIN) via E-Layanan Sains, Badan Riset dan Inovasi Nasional, for their facilities, scientific and technical support. MAM is the primary contributor to this manuscript.

REFERENCES

[1] M. Al-Muttaqii, F. Kurniawansyah, D.H. Prajitno, A. Roesyadi,(2019) 319–327.
[2] N.M.T. Al-Layla, L.A. Saleh, A.B. Fadhil, (2021).
[3] E. Emmanouilidou, A. Lazaridou, S. Mitkidou, N.C. Kokkinos, (2024) 137870.
[4] K. Musa, M. Munirat, J. Jacob, A. Rabiu, K. Dauda, A. Ali, I. Yahuza, (2025) 100201.
[5] L. Marlinda, D.H. Prajitno, A. Roesyadi, I. Gunardi, Y.W. Mirzayanti, M. Al Muttaqii, A. Budianto, (2022) 17–39.
[6] L. Marlinda, M. Al-Muttaqii, I. Gunardi, A. Roesyadi, D.H. Prajitno, (2017) 167–184.
[7] M. Al, D. Annas, I. Yati, H. Hendarsyah, S. Theo, C. Lotebulo, S. Priyanto, A. Aziz, D. Prasetyoko, R. Edra, L. Marlinda,Inorg. (2025) 113855.
[8] A.P.P. Nugroho, 6422-20491-1-Pb, (2014) 2337–3539.
[9] R.- Rasyid, R. Aditya S. W, D. Dian.L, M. Mahfud, A. Roesyadi, (2015) 268–273.
[10] F. Cheng, Z. Wang, X. Cui, L. Li, Z. Shi, S. Liu, S. Yu, J (2023).
[11] R. Ganesan, S. Subramaniam, R. Paramasivam, J.S.M. Sabir, J.S. Femilda Josephin, K. Brindhadevi, A. Pugazhendhi, (2021) 143781. https://doi.org/10.1016/j.scitotenv.2020.143781.
[12] F. Wang, F. Yu, Y. Wei, A. Li, S. Xu, X. Lu, J. https://doi.org/10.1016/j.jaap.2021.105146.
[13] H. Juwono, T. Triyono, S. Sutarno, E.T. Wahyuni, H. Harmami, I. Ulfin, F. Kurniawan, (2017) 337–342. .
[14] H. Chen, S. Fu, L. Fu, H. Yang, D. Chen, (2019) 1–11.
[15] F. González, C. Pesquera, A. Perdigón, C. Blanco, (2009) 7825–7830.
[16] D. Battegazzore, S. Bocchini, J. Alongi, A. Frache, (2014) 54703–54712.
[17] R.E. Nugraha, D. Prasetyoko, N. Asikin-Mijan, H. Bahruji, S. Suprapto, Y.H. Taufiq-Yap, A.A. Jalil, (2021) 110917.
[18] S. Steven, E. Restiawaty, P. Pasymi, Y. Bindar, (2021) 51–57. .
[19] J. Bin Haider, M.I. Haque, M. Hoque, M.M. Hossen, M. Mottakin, M.A. Khaleque, M.A.H. Johir, J.L. Zhou, M.B. Ahmed, M. Zargar, (2022) 135121.
[20] N.A.A. Ismail, M.A. Azmi, S. Ahmad, H. Taib, (2015) 470–474.
[21] R.E. Nugraha, (2023) 31–36.
[22] F. Guo, J. Li, W. Li, X. Chen, H. Qi, X. Wang, Y. Yu, Russ.(2017) 2055–2063.
[23] A. Aziz, B.G. Andini Putri, D. Prasetyoko, R.E. Nugraha, H. Holilah, H. Bahruji, A.A. Jalil, (2023) 32648–32659.
[24] R.E. Nugraha, D. Prasetyoko, N.A. Nareswari, A. Aziz, H. Holilah, H. Bahruji, M.R. Yusop, N. Asikin-Mijan, S. Suprapto, Y.H. Taufiq-Yap, A.A. Jalil, S.W. Purnami, H. Hartati, (2024) 100877.
[25] R.E. Nugraha, D. Prasetyoko, H. Bahruji, S. Suprapto, N. Asikin-Mijan, T.P. Oetami, A.A. Jalil, D.V.N. Vo, Y.H. Taufiq-Yap, (2021) 21885–21896.
[26] K. de Sousa Castro, L. Fernando de Medeiros Costa, V.J. Fernandes, R. de Oliveira Lima, A. Mabel de Morais Araújo, M.C. Sousa de Sant'Anna, N. Albuquerque dos Santos, A.D. Gondim, (2020) 555–564.
[27] H. Hasanudin, W.R. Asri, A. Mara, M. Al Muttaqii, R. Maryana, N. Rinaldi, S. Sagadevan, Q. Zhang, Z. Fanani, F. Hadiah, (2023) 20858–20868.
[28] M. Al Muttaqii, M.P. Marbun, S. Sudibyo, A. Aunillah, D. Pranowo, H. Hasanudin, N. Rinaldi, T.B. Bardant, (2024) 141–148.