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PYROLYSIS OF PALM OIL MILL EFFLUENT (POME) USING MODIFIED LAMPUNG NATURAL ZEOLITE WITH THE SI/AL RATIO OF 1 AS CATALYST

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ABSTRAK

Dalam penelitian ini, limbah pengolahan kelapa sawit yang dikenal sebagai POME dipirolisis menggunakan katalis zeolit alam Lampung (ZAL) yang komposisinya dimodifikasi menjadi nisbah molar Si/Al = 1. Modifikasi dilakukan dengan melarutkan sejumlah tertentu aluminium foil dalam larutan NaOH 1,0 M, lalu dicampur dengan sejumlah tertentu ZAL. Campuran tersebut dihomogenkan dengan menggunakan pengaduk magnetik dan didiamkan pada suhu kamar selama 12 jam untuk proses aging, kemudian dikristalisasi dengan metode hidrotermal pada suhu 100 ºC selama 72 jam. Sampel dikeringkan dan dikalsinasi pada suhu 600 °C selama 6 jam kemudian dikarakterisasi menggunakan teknik X-Ray Diffraction (XRD) dan Scanning Electron Microscope (SEM), hasilnya menunjukkan indikasi pembentukan zeolit-A. Analisis dengan metode Gas Chromatography-Mass Spectrometry (GC-MS) menunjukkan komponen utama BCO yang dihasilkan dari percobaan adalah senyawa hidrokarbon (70%), mencerminakn potensi katalis yang dikembangkan untuk diteliti lebih lanjut.

Keywords: POME, BCO, pirolisis, zeolit alam Lampung, katalis.

ABSTRACT

In this research, palm oil mill effluent (POME), was pyrolized using a modified Lampung natural zeolite (LNZ) catalyst. Modification was conducted by reducing the Si/Al molar ratio to 1 by mixing certain mass of food grade aluminum food dissolved in 1.0 M NaOH solution and certain mass of LNZ. The mixture was homogenized using a magnetic stirrer, left at room temperature for 12 hours, and finally subjected to hydrothermal crystallization at 100 ºC for 72 hours. The solid sample produced was dried and calcined at 600°C for 6 hours then characterized using X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) techniques to evaluate the formation of zeolite-A. The BCO produced from the pyrolysis experiment was analyzed using gas chromatography-mass spectrometry (GC-MS), revealing the presence of hydrocarbon as the main components (70%), suggesting the promising potential of the catalyst for further investigation.

Keywords: POME, pyrolysis, BCO, Lampung natural zeolite, catalyst.

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INTRODUCTION

Demand for energy which continues to increase sharply while fossil fuel reserves continue to deplete is now realized as a serious threat to future energy sustainability. In addition, environmental impacts as a consequence of fossil fuel application are also gaining increased public awareness around the globe. Realizing the increasingly serious problems arising from the use of fossil fuels, development of new and renewable energy sources has become a global effort that continues intensively.

In the context of renewable energy development, biomass-derived fuels (biofuels) are gaining increased interest. one potential that continues to attract interest around the globe. In addition to the availability of renewable raw materials throughout the world, production of biofuels is also supported by the availability of biomass-to-energy conversion technologies which continue to develop and become more mature (Duan *et al.*, 2019; Simanjuntak *et al.*, 2021).

Among various biomass-to-energy conversion technologies, pyrolysis is a method that continues to develop and attracts attention of researchers around the globe. From a raw material perspective, pyrolysis offers a very attractive advantage because it can be applied to process all types of biomass. In addition, pyrolysis does not require complicated equipment, making this technique cost efficient.

The main feature of biomass pyrolysis is production of three types of products, namely gas, liquid, and solid. Of the three products, the liquid product also known as bio crude oil (BCO) has a special value from a new and renewable energy perspective, because it has the potential to replace liquid fuels originating from fossil sources.

Recognizing its potential as a renewable liquid fuel, various studies have been carried out to produce BCO from various raw materials, such as agriculture and industrial wastes (Mo *et al.*, 2022), green algae (Sardi *et al.*, 2022), rice husk (Xu *et al.*, 2019), mixture of solid cassava residue and palm oil (Simanjuntak *et al.*, 2021), mixture of sugar cane bagasse and sludge palm oil (Supriyanto *et al.*, 2018), rice straw (Chen *et al.*, 2019), microalgae (Ganesan *et al.*, 2020), and water hyacinth (Pandiangan *et al.*, 2022).

In Indonesia, various raw materials are available in large quantities, one of them is palm oil mill effluent (POME), which is one of the wastes of palm oil industry. POME is available in very large quantities since palm oil industry is one of the main industries, owned by large companies as well as smallholder industries. Conversion of POME into fuel is also beneficial for environment since this waste is quite resistant to natural degradation. The availability of

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POME and the environmental benefits gained from its treatment are the reasons for choosing this industrial residue as a feedstock in this research.

In application of prolysis technique for biomass treatment, a catalyst is one of the main factors because in addition to lower the temperature it also plays a role in determining the chemical composition of the BCO produced. In appreciating these important roles, various types of catalysts have been used in biomass pyrolysis. Of particular interest are synthetic zeolites for their ability to promote deoxygenation reactions, leading to formation of hydrocarbons (Rabiu *et al*., 2018; Tan *et al*., 2013; Garba *et al*., 2018)

In our previous research (Simanjuntak *et al*., 2021) we reported successful synthesis of zeolite-A (with the Si/Al ratio of 1) from rice husk silica and aluminum foil and its application as a catalyst for pyrolysis of biomass mixtures. The results obtained show that zeolite-A synthesized has high performance, producing BCO with a hydrocarbon content of more than 90%. Despite its high performance, one note that must be acknowledged is that the synthesis process requires a relatively long time, especially for the extraction of silica from rice husks.

In an effort to shorten the synthesis process, in this research, Lampung natural zeolite (LNZ) which has a Si/Al ratio of 6.4 was modified to have a Si/Al ratio of 1 with the addition of aluminum (using aluminum foil). The modified LNZ was characterized by X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) and then used as a catalyst for pyrolysis of POME.

METHOD

Tools and Materials

Materials used in this study were Lampung natural zeolite (LNZ) purchased from local supplier, food grade aluminum foil (FGAF), reagent grade NaOH, and Palm Mill Oil Effluent (POME) obtained from local palm oil company.

The main equipments used are Teflon lined hydrothermal autoclave, oven, furnace, and laboratory scale pyrolysis reactor. XRD characterization of the sample was conducted using PANanalytical type EMPYREAN instrument, characterization using SEM was carried out using Zeiss EVO® MA 10 instrument, and GC-MS analysis was carried out using QP2010 SE SHIMADZU instrument. Identification of chemical components of the BCO was carried out with the aid of MS Library System NIST12.LIB and WILEY229.LIB.

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Procedure

As previously mentioned, modification of LNZ was aimed at changing the Si/Al ratio to 1. For this purpose, a typical experiment was conducted by dissolving 29.68 g FGAF in 150 mL of 1.0 M NaOH solution. Into the solution, a mass of 50 g of LNZ was added and the mixture was homogenized using a magnetic stirrer, then left at room temperature for 12 hours for aging process. After the aging process was complete, the mixture was transferred into hydrothermal autoclave and placed in an oven for crystallization at 100 ºC for 72 hours. After the completion of crystallization process, the mixture was filtered and the solid was dried in an oven at 100 ºC for 8 hours. The solid was then ground into powder and sieved with a 300 mesh sieve to obtain a sample with a relatively homogeneous particle size, and finally subjected to calcination treatment at 550 ºC for 6 hours. For comparison, the original LNZ sample was also subjected calcination at the same condition. The two samples were then characterized using XRD and SEM techniques, and finally, they were used as catalyst in pyrolysis experiments.

Pyrolysis experiment was run using laboratory scale pyrolysis reactor. The reaction mixture consists of 250 mL POME and 12.5 g catalyst was transferred into reactor. The reactor was heated and condensed liquid was collected for 45 minutes. The liquid was transferred into a separating funnel and left for 24 hours to allow the separation between the water and the organic phase (BCO). Both the original and modified LNZ were used as catalysts and the BCO samples produced were analyzed using the GC-MS method to identify the chemical components of the samples.

RESULTS AND DISCUSSION

Characterization of Zeolite Used Oil

To evaluate the changes that occurred as a result of the composition modification made, the original and modified LNZ samples were characterized using XRD and SEM. The XRD diffractogram of the samples with the phases composing the samples identified with the aid of Match!3 version 2.4.7 software are shown in Figure 1.

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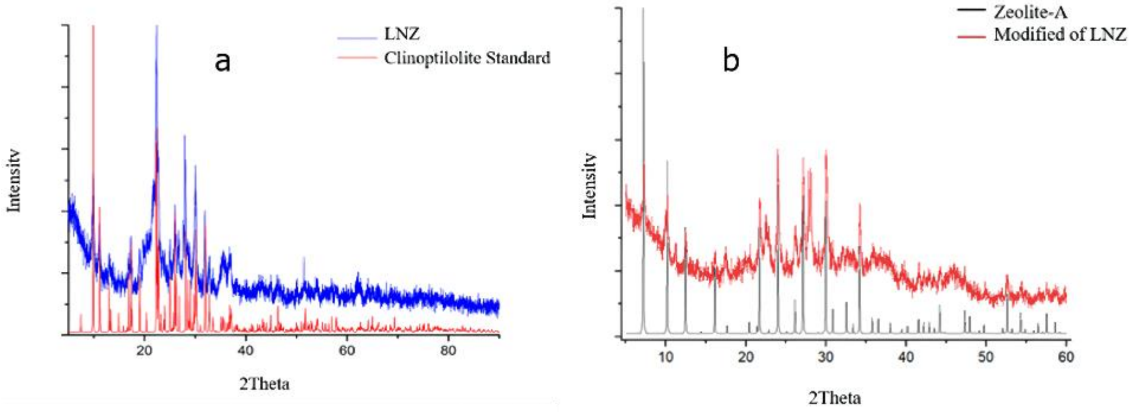

Figure 1. XRD diffractograms of original LNZ (a) and modified LNZ (b)

The XRD diffractograms presented in Figure 1 show the existence of amorphous and crystalline phases in both samples. With the help of software (Match! 3 version 2.4.7) it was found that LNZ (Figure 1a) is clinoptilolite, which is one type of natural zeolite commonly found. Comparing the two diffractograms, some differences can be observed, in which the diffractogram of the modified LNZ is marked by the appearance of a diffraction peak at 2° at around 7°, while in the initial LNZ diffractogram, this peak is not found. In addition, the diffraction peaks at 2° at around 10° and 12° which are the main diffraction peaks in the initial LNZ, almost disappeared in the modified LNZ diffractogram. With the help of the software, it was found that the diffraction pattern of the modified LNZ is to some extent similar to that of standard zeolite-A. These results indicate that in the modified LNZ, zeolite-A has been formed, although it should be acknowledged that complete transformation of LNZ into zeolite-A has not been achieved.

As can be seen in Figure 2, the two samples display quite obviously different surface morphology, demonstrating that the modified LNZ has significantly higher crystallinity. In addition, the sample is also characterized by a much evident particle shape in the form of a cube, which is a typical shape of zeolite-A particle (Simanjuntak et. al 2021).

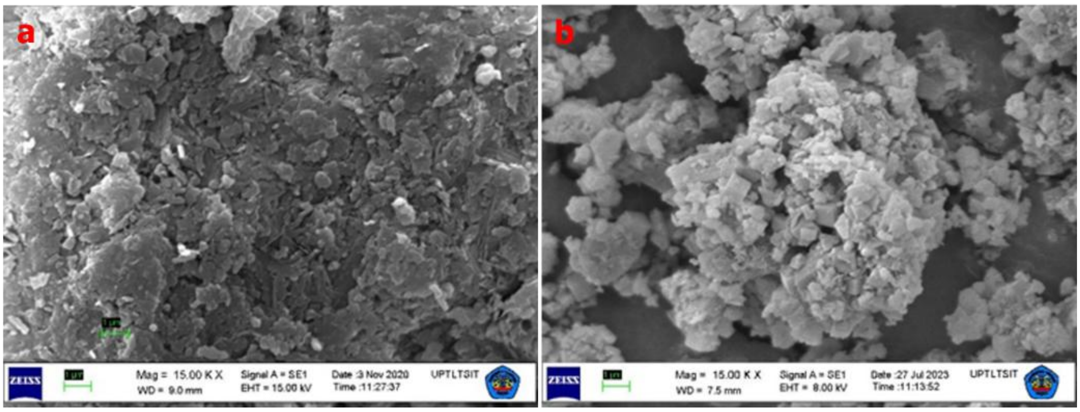

Figure 2. SEM micrographs of the samples investigated (a) original LNZ and (b) modified

GC-MS Analysis of *Bio Crude Oil* (BCO)

To identify the chemical components composing the BCO produced with the use of original and modified LNZ as catalyst, the samples were analyzed using the GC-MS technique. The GC chromatograms of the samples are compiled in Figure 3. As can be observed, the chromatograms display quite similar patterns which suggests that the two samples are composed of mostly the same compounds. For a more detailed comparison, the chemical components of the samples are presented in Table 1.

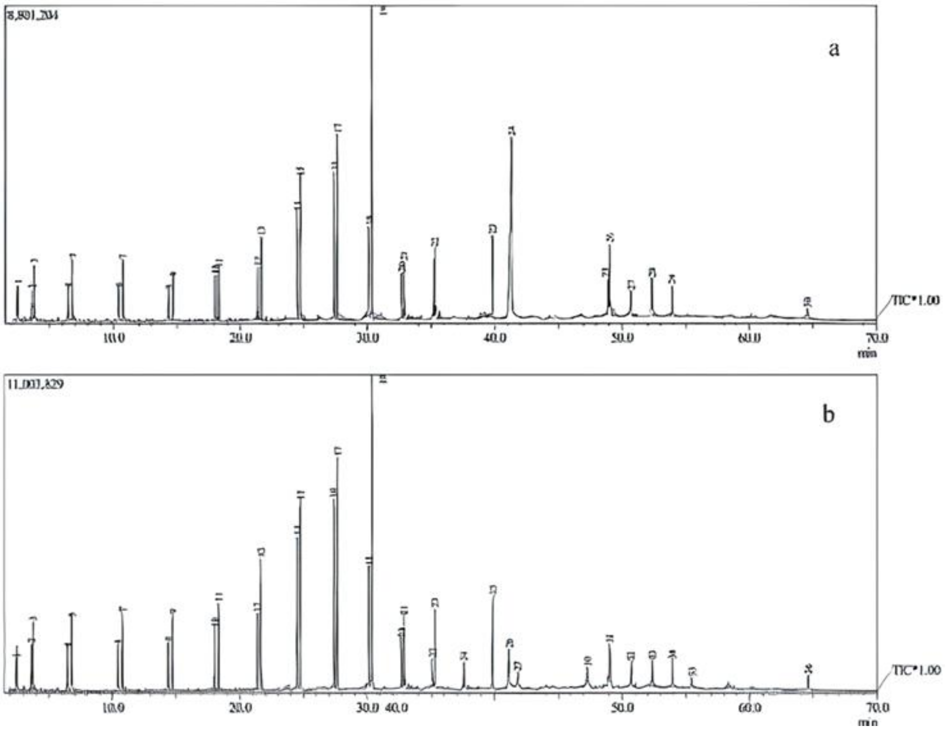

Figure 3. GC-chromatogram of the BCO produced using original LNZ (a) and modified LNZ (b) as catalyst

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Table 1. Chemical components of BCO are produced using original and modified LNZ as catalyst

No.	Molecular formula	Compound name	Relative percentage (%)		Category
			Original LNZ	Modified LNZ	
1	C_6H_{12}	1-Hexene	1.63	1.31	Hydrocarbon
2	C_7H_{14}	1-Heptene	1.17	0.99	Hydrocarbon
3	C_7H_{16}	Heptane	1.83	1.54	Hydrocarbon
4	C_8H_{16}	1-Octene	1.52	1.21	Hydrocarbon
5	C_8H_{18}	Octane	2.42	1.97	Hydrocarbon
6	C_9H_{18}	1-Nonene	1.55	1.16	Hydrocarbon
7	C_9H_{20}	Nonane	2.53	1.83	Hydrocarbon
8	$C_{10}H_{20}$	1-Decene	1.55	0.91	Hydrocarbon
9	$C_{10}H_{22}$	Decane	2.15	1.29	Hydrocarbon
10	$C_{11}H_{22}$	1-Undecene	1.92	1.26	Hydrocarbon
11	$C_{11}H_{22}$	4-Undecene	-	1.56	Hydrocarbon
12	$C_{11}H_{24}$	Undecane	2.57	-	Hydrocarbon
13	$C_{12}H_{24}$	1-Dodecane	2.23	1.44	Hydrocarbon
14	$C_{12}H_{26}$	Dodecane	3.61	2.31	Hydrocarbon
15	$C_{14}H_{28}$	1-Tetradecene	6.19	3.38	Hydrocarbon
16	$C_{13}H_{28}$	Tridecane	5.84	4.03	Hydrocarbon
17	$C_{13}H_{26}$	1-Tridecene	4.93	1.46	Hydrocarbon
18	$C_{15}H_{30}$	1-Pentadecene	4.05	-	Hydrocarbon
19	$C_{15}H_{32}$	Pentadecane	10.89	-	Hydrocarbon
20	$C_{16}H_{34}$	Hexadecane	2.51	5.22	Hydrocarbon
21	$C_{14}H_{28}$	1-Tetradecene	1.85	2.83	Hydrocarbon
22	$C_{17}H_{36}$	Heptadecane	2.65	10.18	Hydrocarbon
23	$C_{16}H_{32}$	1-Hexadecene	1.85	1.5	Hydrocarbon
24	$C_{14}H_{30}$	Tetradecane	7,59	2,13	Hydrocarbon
25	$C_{17}H_{34}$	1- Heptadecene	0.95	-	Hydrocarbon
26	$C_{20}H_{42}$	Eicosane	0.83	2.5	Hydrocarbon
27	$C_{17}H_{34}O$	2- Heptadecanone	-	2.87	Ketone
28	$C_{14}H_{28}O_2$	Tetradecanoic acid	-	16.27	Acid
29	$C_{20}H_{42}O$	1-Eicosanol	-	1.27	Alcohol
30	$C_{20}H_{42}$	Nonadecane	3.43	-	Hydrocarbon
31	$C_{12}H_{24}O$	2-Dodecanon	2.30	-	Ketone
32	$C_{18}H_{36}O$	3 - Dodecanone	0.96	-	Ketone
33	$C_{18}H_{36}O$	7 - Octadecanone	1.04	-	Ketone
34	$C_{18}H_{36}O$	9 - Octadecanone	1.35	-	Ketone
35	$C_{13}H_{24}O_2$	2-propenyl diaconate	1.33	-	Acid
36	$C_{13}H_{26}O_2$	Tridecanoic acid	1.16	-	Acid
37	$C_{21}H_{42}O$	11-Heneicosanone	0.50	2.89	Ketone
38	$C_{27}H_{56}O$	1-Heptacosanol	2.48	1.37	Alcohol
39	$C_{18}H_{36}O$	8-Octdecanone	-	1.32	Ketone
40	$C_{17}H_{36}O$	10-Nonadecanone	-	1.21	Ketone
41	$C_{19}H_{36}O_2$	Octadecanoic acid	1.00	0.60	Acid

As shown in Table 1, the components of both samples consist of mostly the same compounds and are dominated by the hydrocarbon group. Apart from this main component, compounds were also found in relatively smaller amounts, namely acid, ketone, ester, and alcohol, as shown in Table 2. The presence of different chemical groups composing BCO is acknowledged as general characteristic of BCO regardless of the raw materials treated, as has been reported by other workers (Mullen *et al*., 2010; Mohammed *et al*., 2016; Simanjuntak *et al*., 2017).

The presence of hydrocarbon compounds (biohydrocarbon) as the main component of the BCO produced is an important finding because they can be used as a substitute for hydrocarbon fuels originated from petrochemical sources.

Based on the length of carbon chains, biohydrocarbons can be classified into biogasoline (C_5-C_{12}), biokerosene (C_{13}-C_{17}), and biodiesel (C_{18}-C_{28}). The distribution of the three groups of biohydrocarbons can be seen in Table 2, displaying that in both BCO samples produced, biogasoline is the main fraction followed by bioavture and biodiesel as the fraction with the lowest percentage.

Table 2. Chemical composition of BOC produced with the use of original and modified LNZ as catalyst

Catalyst	**Hydrocarbon (%)**				**Acid**	**Ketone**	**Alcohol**	**Ester**
	$C_6 – C_{12}$	**$C_{13} – C_{17}$**	**$C_{18} – C_{28}$**	**Total**				
Original LNZ	38.23	26.47	2.93	67.64	8.82	17.64	2.94	0
Modified LNZ	43.33	23.33	3.33	69.99	3.33	10.00	10.00	3.33

In terms of total biohydrocarbons, the difference between BCO produced with original LNZ and modified LNZ is not very significant, but the reduction in acid and ketone levels, which are undesirable components, is quite significant with the use of modified LNZ, although, for alcohols and esters, the opposite is true.

CONCLUSION

The results of this research show that it is possible to convert natural zeolite into zeolite-A by adjusting the Si/Al ratio using food grade aluminum foil. Although total transformation of natural zeolite has not been achieved, indications of the formation of zeolite-A are shown quite clearly by XRD and SEM data.

The results of the pyrolysis experiment show that the use of both zeolites as catalysts produces BCO with hydrocarbon compounds as the main component. Although the difference is not significant, the biohydrorabon content of the BCO produced with the use of modified LNZ is slightly higher, but significant reductions in acid and ketone contents were observed.

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REFERENCES

Chen, D., Wang, Y., Liu, Y., Cen, K., Cao, X., Ma, Z., and Li, Y. (2019). Comparative Study on the Pyrolysis Behaviors of Rice Straw under Different Washing Pretreatments of Water, Acid Solution, and Aqueous Phase Bio-oil by Using TG-FTIR and PY-GC/MS. *Fuel*, 252, 1–9. https://doi.org/10.1016/j.fuel.2019.04.086

Duan, D., Zhang, Y., Lei, H., Villota, E., and Ruan, R. (2019). Renewable Jet- fuel Range Hydrocarbons Production from Co-pyrolysis of Lignin and Soapstock with the Activated Carbon Catalyst. *Waste Management* 88:1-9. https://doi.org/10.1016/j.wasman.2019.03.030

Ganesan, R., Manigandan, M. S., Samuel, R. Shanmuganathan, K. Brindhadevi, N. T. L. Chi, P., Duc, A., and Pugazhendhi, A. (2020). A Review on Prospective Production of Biofuel from Microalgae. *Biotechnology Report*, 27, 1-13. https://doi.org/10.1016/j.btre.2020.e00509

Garba, M.U., Musa, U., Olugbenga, A.G., Mohammad, Y.S., Yahaya, M., and Ibrahim, A.A. (2018). Catalytic Upgrading of Bio-oil from Bagasse: Thermogravimetric Analysis and Fixed Bed Pyrolysis. *Beni-Suef University Journal of Basic and Applied Sciences*, 7, 776–781. https://doi.org/10.1016/j.bjbas.2018.11.004

Mo, W., Xiong, Z., Leong, H., Gong, X., Jiang, L., Xu, J., Su, S. Hu, S., Wang, Y., and Xiang, J. (2022). Processes Simulation and Environmental Evaluation of Biofuel Production via Co-Pyrolysis of Tropical Agricultural Waste. *Energy*, 242, 123016. https://doi.org/10.1016/j.energy.2021.123016

Mohammed, I.Y., Kazi, F.K., Yusup, S., Alaba, P.A, Sani, Y.M., and Abakr, Y.A. (2016). Catalytic Intermediate Pyrolysis of Napier Grass in a Fixed Bed Reactor with ZSM-5, HZSM-5 and Zinc-Exchanged Zeolite-A as the Catalyst. *Energies*, 9(246), 1-17. https://doi.org/10.3390/en9040246

Mullen, C.A., Boateng, A.A., Hicks, K.B., Goldberg, N.M., and Moreau, R.A. (2010). Analysis and Comparison of Bio-Oil Produced by Fast Pyrolysis from Three Barley Biomass/Byproduct Streams. *Energy and Fuels*, 24, 699–706. https://doi.org/10.1021/ef900912s

Pandiangan, K.D., Simanjuntak, W., Avista, D., Arinanda, A.G., Hadi, S., and Amrulloh, H. (2022). Synthesis of Hydroxy-Sodalite from Rice Husk Silica and Food-Grade Aluminum Foil as A Catalyst for Biomass Pyrolysis. *Trends in Sciences*, 19(20), 1-11. https://doi.org/10.48048/tis.2022.6252

Rabiu, S.D., Auta, M., Kovo, A.S. (2018). An Upgraded Bio-Oil Produced from Sugarcane Bagasse Via the Use of HZSM-5 Zeolite Catalyst. *Egyptian Journal of Petroleum*, 27, 589-594. https://doi.org/10.1016/j.ejpe.2017.09.001

Sardi, B., Ningrum, R.F., Ardiansyah, V.A., Qadariyah, L., and Mahfud, M. (2022). Production of Liquid Biofuels from Microalgae Chlorella sp. via Catalytic Slow Pyrolysis. *International Journal of Technology*, 13(1), 147-156. https://doi.org/10.14716/ijtech.v13i1.4358

Simanjuntak, W., Sembiring, S., Pandiangan, K.D., Pratiwi, E., and Syani, F. (2017). Hydrocarbon Rich Liquid Fuel Produced by Co-Pyrolysis of Sugarcane Bagasse and Rubber Seed Oil Using Aluminosilicates Derived from Rice Husk Silica and Aluminum Metal As Catalyst. *Oriental Journal of Chemistry*, 33, 3218-3224. https://doi.org/10.13005/ojc/330669

Simanjuntak, W., Pandiangan, K.D., Sembiring, Z., Simanjuntak, A., and Hadi, S. (2021). The Effect of Crystallization Time on Structure, Microstructure, and Catalytic Activity of Zeolite-A Synthesized from Rice Husk Silica and Food-Grade Aluminum Foil. *Biomass and Bioenergy*, 148(106050),1-7. https://doi.org/10.1016/j.biombioe.2021.106050

Supriyanto, R., Simanjuntak, W., Pandiangan, K.D., Situmeang, R.T.M., and Ahmadhani, M.Y. (2018). Chemical Composition of Liquid Fuel Produced by Co-pyrolysis of Sugarcane Bagasse and Sludge Palm Oil Using Zeolite-Y as Catalyst. *Oriental Journal of Chemistry*, 34(3), 1533-1540. http://dx.doi.org/10.13005/ojc/340345

Tan, S., Zhang, Z., Sun, J., and Wang, Q. (2013). Recent Progress of Catalytic Pyrolysis of Biomass by HZSM-5. *Chinese Journal of Catalysis*, 34, 641-650. https://doi.org/10.1016/s1872-2067(12)60531-2

Xu, C., Wang, H., Li, X., Zhou, W., Wang, C., and Wang, S. (2019). Explosion Characteristics of a Pyrolysis Biofuel Derived from Rice Husk. *Journal of Hazardous Materials*, 369, 324-333. https://doi.org/10.1016/j.jhazmat.2019.01.101

http://dx.doi.org/10.23960/analit.v9i02.199