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The Effect of Acid Activated Natural Zeolite Catalyst on Further Catalytic Cracking of Liquid Product's Heavy Fraction from Plastic Waste Treatment Factory

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ABSTRACT

The influence of activated natural zeolite catalyst on the further cracking of liquid product's heavy fraction from plastic waste treatment factory been studied resulting in alternative fuel oil. Natural zeolite from Wonosari, Yogyakarta was activated with 1 M H2SO4 solution. Natural zeolite and activated zeolite were characterized using XRD at an angle of 2θ=5-60 degrees. Further cracking process was carried out to study the ratio of catalyst mass of 25 g; 50 g; 75 g; 100 g to 750 mL weight fraction of the factory liquid product. The further cracking product was flame tested, specific gravity measured by gravimetric method and characterized using GC-MS. The calculation of the constituent fuel fractions is also carried out. The performance test of the further cracking product as an alternative fuel was carried out for the generator engine ignition process. The result showed that the activation process using acid was not destroy the zeolite structure. The study of ratio catalyst to liquid waste volume obtained an optimum result at 50 g/750 mL based on the volume of resulted fuel oil with small amount of catalyst. The resulted fuel oil has a density of 0.7908 g/mL with a clear yellow color, and flammable. The GC-MS analysis resulted in fuel oil consisting of 4.11% gasoline, 8.42 kerosene, 75.56% solar, and 11.93% heavy fraction

Keyword: *plastic waste, advanced cracking, active zeolite*

1. INTRODUCTION

The total production of plastic waste globally in 2011 has reached 280 million tons and continues to increase at a rate of 4% per year in 2016 (Sriningsih, et al, 2014). Based on statistical data, Indonesia contributes 3.6 million tons of plastic waste per year (Jambeck, et al, 2015). Plastic waste is the least biodegradable material and stay long in the environment for hundreds of years (Ashworth, et al, 2014). Conventional recycling methods such as sorting and shredding can only recycle about 15-20% of the total plastic waste (Khan & Kaneesamkandi, 2013). One of the plastic waste processing that has recently been developed by processing the waste become an alternative energy. The pyrolysis method processes plastic waste into oil, solid residue (char) and gas at a temperature of 300-900°C through thermal decomposition. However, conventional thermal pyrolysis has limitations because it is very temperature dependent (Borsodi, et al, 2011). Liquid oil resulting from thermal pyrolysis of plastic waste contains impurities and residues (Sadaf, et al, 2018) . Furthermore, thermal pyrolysis of polyethylene (PE) plastic waste such as high density polyethylene (HDPE) and low density polyethylene (LDPE) together with polypropylene (PP) are difficult because of the hydrocarbon chain structure branched (Achilias, et al, 2007). To overcome this problem, many catalytic pyrolysis processes have been developed (catalytic cracking).

Utilization of plastic waste into fuel is one of the popular solutions to handle the abundant of plastic waste. The research that was successfully carried out by Krimadi (2013) in processing PP type plastic waste using a natural zeolite catalyst produced a liquid with fuel characteristics. It was also reported that processing HDPE type plastic waste in the form of oil packaging bottles with natural zeolite has a relatively better catalytic activity than natural clay (Lestari, 2014). Meidy, et al. (2016) has succeeded in further cracking the liquid product with natural zeolite producing a clear yellow liquid product, which has a specific gravity equivalent to gasoline. However, these studies involved only a relatively small number of samples (only in the range of grams to several Kg). Wasini, et al (2019) reported that processing the HDPE resulted in an oil liquid dominated by the heavy oil fraction so it cannot directly be used as fuel for motor vehicles. This liquid product can be further processed into more valuable fractions, namely the gasoline and solar fractions. This further process involves heat and the use of a catalyst with special properties from acid-activated natural zeolite. H_2SO_4 solution in a certain concentration is commonly used to activate solid catalysts. The pore cleaning of the solid catalyst was done using the acid to increase the acid site, which is believed contribute to the more active catalyst performance.

2. RESEARCH METHOD

Natural Zeolite Activation and Characterization

Natural zeolite was sieved using a 200 mesh sieve. A total of 300 g of natural zeolite was mixed with 500 mL of 1 M H_2SO_4 at a temperature of 60-70°C for 3 hours under stirring. The solution was then filtered and washed with distilled water until neutral pH. The natural zeolite was dried at temperature of 105°C for 3 hours. The natural zeolite before and after activation was characterized using XRD at an angle of $2\theta = 5–60^o$.

Advanced Catalytic Cracking of Factory Weight Fraction Products

The weight fraction of residual oil from the distillation of plastic fuel products as much as 750 mL was mixed with 25 grams of activated natural zeolite in a catalytic cracking reactor. The reactor is heated until droplets of liquid product are formed and stopped when there are no drops in the reservoir bottle. A study of weight variations of activated natural zeolite catalysts of 50, 75 and 100 g was conducted for every 750 mL of the sample weight fraction.

Advanced Catalytic Cracking Oil Characterization

The characterizations carried out in this study were flame test, determination of specific density and analysis using GC-MS for the resulted, process residues, and the weight fraction.

Advanced Catalytic Cracking Oil Performance Test

The oil resulting from further catalytic cracking as much as 100 mL was put into the generator fuel reservoir. The generator is turned on and the length of time the generator engine can run is measured. The results of this test are compared with the results of performance tests using fuels on the market (premium gasoline and pertalite).

3. RESULTS AND DISCUSSION

Natural Zeolite Activation

The influence of acid activation toward natural zeolite was analyzed using X-Ray Diffractometer (XRD) as shown in Figure 1.

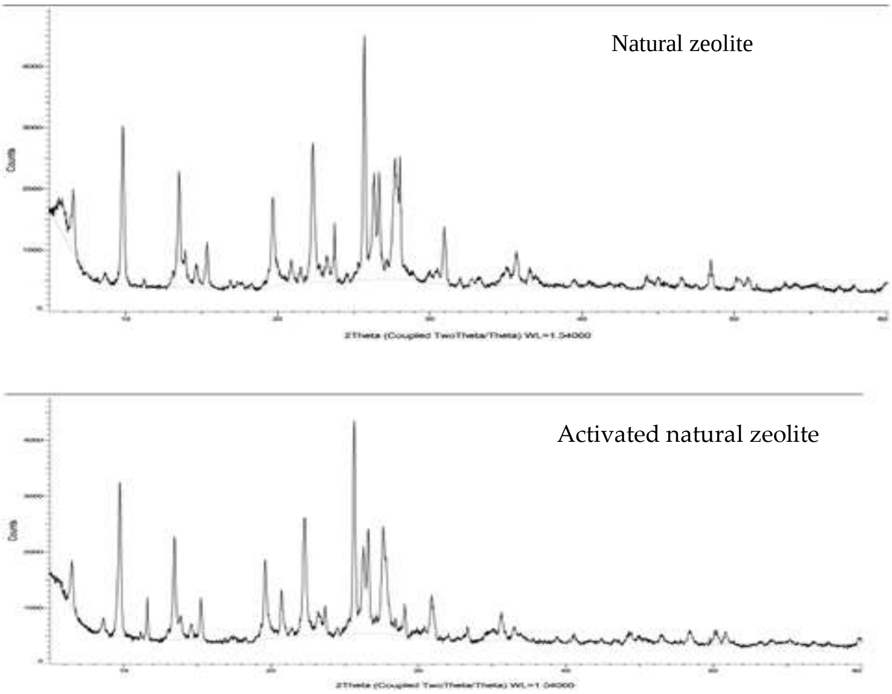


Figure 1. The diffractogram of Wonosari natural zeolite before (up) and after (down) acid activation

Figure 1 indicated that activation using 1 M H_2SO_4 did not change the zeolite structure, and the diffractogram of the natural zeolite before and after activation process are quite similar. Sharp peaks that indicated a good crystallinity of the minerals were found in both samples. Natural zeolite from Wonosari contains a lot of minerals mordenite and clinoptilotite[12]. The concentration of 1 M H_2SO_4 has optimum since the higher concentration might resulted in a crystal damage. The mechanism of the activation process was started by the dissolution of metal ions to fill the zeolite cavities/pores and then replaced by H^+ ions from acid. According to Ertan[13], the acid activation causes cations exchange that usually exist in natural zeolite pores (eg K^+, Na^+) with H^+ from the acid. The process of replacing ions with H^+ ions lead the acidity of the active zeolite increase compared to the original zeolite. The activated zeolite was then used as a catalyst in the re-cracking process of liquid plastic waste processing into fuel.

Further catalytic cracking process

One of the important parameters in the cracking process is the ratio of catalyst weight to oil volume. In this study, 4 variations were carried out, namely: 25 g/ 750 mL; 50 g/ 750 mL; 75 g/750 mL and 100 g/750 mL respectively. The end of the reaction was determined when no more droplets were formed in the product container bottle. The results of further cracking with the study of variations in the ratio of catalyst weight/volume weight fraction are presented in Table 1.

Table 1. Percentage of advanced catalytic cracking products

No.	Activated zeolite mass (g)/ sample volume (mL)	Products percentage (%)		
		liquid	gas	rest
1	25/750	67.54	6.58	25.88
2	50/750	77.02	7.31	15.67
3	75/750	75.08	7.58	7.34
4	100/750	80.29	9.18	10.53
	control	27.35	0.80	71.85

Table 1 indicated that further cracking process resulted in three products, namely, a clear yellow liquid product, a brown liquid waste product, and a gas product. The effectiveness of the catalyst use is measured by the volume of the liquid product against the weight of the catalyst used as shown in Table 2.

Table 2. Comparison of advanced cracking liquid products

No	Mass of activated zeolite (g)	Volume (mL)	Volume of cracking product (mL)	Color
1	25	750	510	clear yellow
2	50	750	580	clear yellow
3	75	750	575	clear yellow
4	100	750	650	clear yellow
5	control	750	210	slightly brown yellow

Table 2 showed that the use of active zeolite catalyst has given a significant increase in liquid product when compared to inactivated natural zeolite catalysts. The greater amount of catalyst used tends to the increase of resulted oil product. However, increasing the use of catalyst after 50 g did not give a significant increase in liquid product. On the other hand, the principle of using a catalyst is as little as possible to produce the desired product maximally. Therefore, the optimal condition chosen for this research is the ratio of catalyst weight/volume to weight fraction, which is 50 g/750 mL.

The color comparison between the weight fraction of the mill, the result of further cracking and the rest of the further cracking are shown in Figure 2, which indicated that the further cracking process have successfully convert the heavy fraction of the milled product to a relatively small molecule with a clear colour. However, the data also showed that there are some residue from the further cracking process as a liquid with a darker color and higher viscosity.

Figure 2. Color comparison between the weight fraction of the mill, the result of further cracking and the rest of the further cracking

Advanced Catalytic Cracking Product Characterization

There are 3 characterization methods that used to analyze the resulted liquid products of this advanced catalytic cracking:

1. Flame Test.

Tissue paper was dropped by the fuel liquid sample when ignited together with the comparison of highly flammable tissue and were given a great flame. The contribution of fuel given to the flame is qualitatively very real when compared to the flame of the flammable tissue flame.

2. Determination of Specific gravity

Specific gravity measurements were carried out gravimetrically using a pycnometer. The results of the measurement of specific gravity of the data are presented in Table 3.

Table 3. Specific gravity values of catalytic cracking products and commercial fuels

No	Sample	Density (g/mL)
1	Catalytic recracking product #1 (25 g)	0.7918
2	Catalytic recracking product #2 (50 g)	0.7908
3	Catalytic recracking product #3 (75 g)	0.7898
4	Catalytic recracking product #4 (100 g)	0.7891
5	Bensin Premium	0.7259
6	Solar	0.8562
7	Minyak Tanah	0.8157
8	Fraksi berat produk cair pabrik	0.8065

Table 3 shows that the further catalytic cracking product has a lower specific gravity than the processed weight fraction. This is also evidence that the cracking changed the large molecules into smaller ones. However, all further cracking products are still larger than the specific gravity of gasoline. It is might because the cracking process has not been selective in forming the gasoline fraction so the further catalytic cracking process has not yet occurred optimally. The density of the advanced cracking product is about 0.7891-0.7918 g/mL that range between the specific gravity of gasoline (0.7259 g/mL) and diesel fuel (0.8562 g/mL) so it can be predicted the resulted liquid contain a mixture of gasoline and diesel fractions.

Analysis of Advanced Catalytic Cracking Products Using Gas Chromatography-Mass Spectrometry

To ensure that the cracking process has occurred, the GC-MS analysis were done toward the heavy fraction of plastic waste, the oil product of further cracking, and the residue of further cracking and racterization is carried out on the weight fraction of the factory product, the results of further cracking and the rest of the further cracking, the results of which are shown in Figure 3.

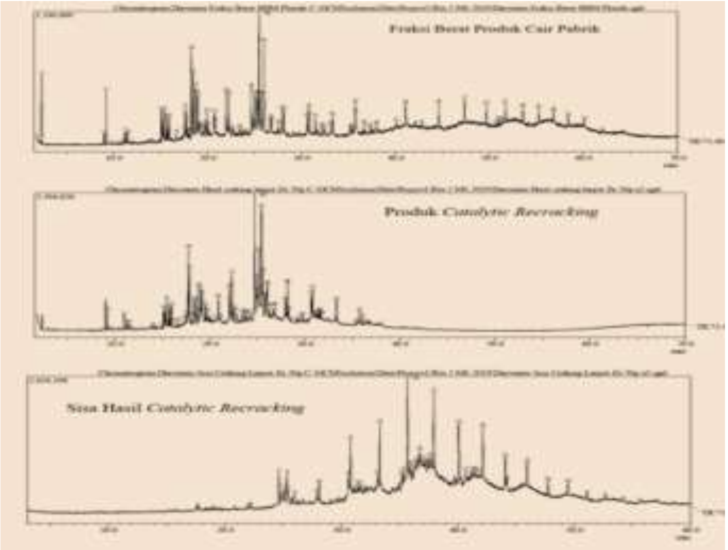


Figure 3. Chromatogram of the weight fraction of factory liquid products, catalytic re-cracking products and residual catalytic re-cracking

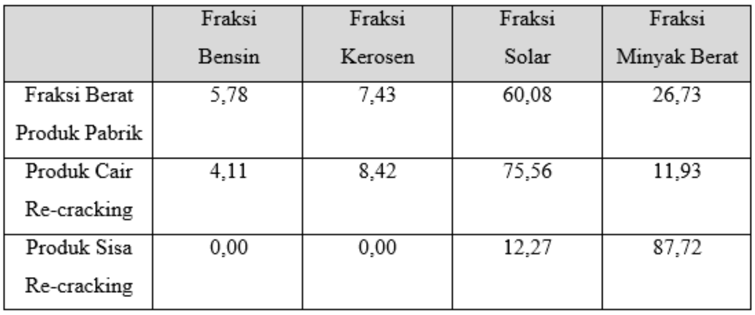
Based on Figure 3, the chromatogram of the initial sample or the weight fraction of the factory liquid product shows that the liquid is a mixture of 82 compounds as evidenced by the presence of 82 measured peaks. These peaks appear in the retention time range of 2,328 – 60.089 minutes. Qualitatively, the chromatogram shows that the heavy fraction contains a small amount of gasoline making up hydrocarbons (tR < 12 minutes) and is dominated by the diesel fraction (tR 17.505 minutes

– 28.118 minutes) and heavy oil fractions (tR 30.594 minutes – 60.089 minutes). This means that the main component is still a mixture of large molecules so that it requires a further cracking process (re-cracking) to produce small molecules as constituents of more valuable fractions. The re-cracking process uses an active zeolite catalyst by studying the ratio of the best catalyst weight/volume weight fraction at 50 g/750 mL. The re-cracking product is a clear yellow liquid, some of it is gas and the rest is a dark brown viscous liquid.

Figure 3 also showed that the chromatogram of the catalytic re-cracking product is qualitatively a mixture of 63 compounds as evidenced by the appearance of 63 detected peaks. It has been seen a shift in the appearance of peaks to a smaller retention time when compared to the weight fraction chromatogram of the manufactured product. This indicates that a further cracking process has occurred to produce smaller molecules. Meanwhile, based on the chromatogram, the rest of the re-cracking product was qualitatively a mixture of 43 compounds as evidenced by the appearance of 43 detected peaks. Peaks appear at relatively large retention times indicating the presence of large molecules that cannot be broken down into simpler molecules. This is confirmed by the increasing viscosity and the darker the color.

Too determine the composition of the fuel fraction from the initial sample, the re-cracking liquid product and the residu of the re-cracking, calculations were made based on GC-MS data (retention time and peak area). By referring to the standard GC-MS BBM data (gasoline, kerosene and diesel), it can be calculated the percentage of each fraction whose results are given in Table 4, which confirmed the previous data that the further cracking process with activated zeolite catalyst has occurred. This is evidenced by the decrease in the percentage of heavy oil fraction data from 26.73% (in the rest of the factory products) to 11.93% (in the advanced cracking liquid product). The decrease was followed by an increase in the percentage of the diesel fraction (60.08 to 75.56%) and the kerosene fraction (7.43 to 8.42%) between the initial sample and the re-cracking product. This phenomenon shows that although further cracking has occurred, it has not been able to be directed to the gasoline fraction as a more valuable fraction, but the selectivity is still directed towards diesel products. The decrease in the gasoline fraction data is possible that the use of heat in the re-cracking stage actually releases the gasoline fraction in the initial sample.

Table 4. The percentage composition of fuel fractions in the weight fraction of factory products, re-cracking liquid products and re-cracking residues

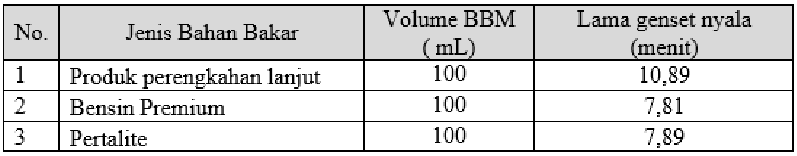


	Fraksi Bensin	Fraksi Kerosen	Fraksi Solar	Fraksi Minyak Berat
Fraksi Berat Produk Pabrik	5,78	7,43	60,08	26,73
Produk Cair Re-cracking	4,11	8,42	75,56	11,93
Produk Sisa Re-cracking	0,00	0,00	12,27	87,72

Testing the Performance of Liquid Products Resulting from Advanced Catalytic Cracking in Genset Engines

To prove that the re-cracking liquid product has the character of BBM and has performance in starting the engine, a test is carried out to start the generator engine. Tests controlled with comparable market fuels. The test results are given in the data Table 5, which showed that the liquid product of re-cracking from the liquid product of the plastic waste processing plant can start the generator engine properly. Based on the data, its performance is very competitive compared to the equivalent fuel on the market. In fact, the data shows that re-cracking products take longer to run the engine, which means they are more efficient. This phenomenon is probably because the cracking product is proven to be dominated by the diesel fraction where the constituent molecules are relatively larger than the gasoline fraction. So that it takes longer to experience the combustion process in the engine carburetor. Liquid re-cracking products are more efficient, as evidenced by the longer time to start the generator engine, which is 10.89 minutes compared to premium gasoline which is only 7.81 minutes and pertalite is only 7.89 minutes for every 100 mL of use. This is probably because the liquid product of advanced cracking contains molecules that are larger than the molecules that make up premium gasoline and pertalite so that it is slower when combustion occurs in the engine. These data further confirm that fuel from plastic waste processing has bright prospects as an alternative fuel to replace conventional fuel.

Table 5. Performance test of re-cracking products and commercial fuels



No.	Jenis Bahan Bakar	Volume BBM (mL)	Lama genset nyala (menit)
1	Produk perengkahan lanjut	100	10,89
2	Bensin Premium	100	7,81
3	Pertalite	100	7,89

4. CONCLUSION

It can be concluded that the acid activation of natural zeolite from Wonosari using 1 M H2SO4 increased the active site of the zeolite, which increase the liquid yield of liquid product when the activated zeolite was applied in the further catalytic cracking of liquid plastic waste at amount of 370 mL (176%). The ratio of the weight of activated zeolite to the volume of the weight fraction of the factory liquid product which was optimum in the advanced cracking process was 50 g/750 mL to produce 580 mL of liquid product with a clear yellow color, flammable, specific gravity 0.7908 g/mL and dominated by the solar fraction. The advanced catalytic cracking product is able to start the generator engine for 10.89 minutes and is more efficient than market fuel which is equivalent to premium gasoline (7.81 minutes) and pertalite (7.89 minutes) for 100 mL of use.

REFERENCES

Achilias,D.S.,Roupakias,C., Megalokonomos,P., Lappas,A.A. and Antonakou,E.V., (2007), Chemical recycling of plastic wastes made from polyethylene (LDPE and HDPE) and polypropylene (PP), *J. Hazard Mater*. 149, 536-542

Ashworth, D.C., Elliott,P., Toledano,M.B., (2014), Waste incineration and adverse birth and neonatal outcomes : a systematic review, *Environ. Int*. 69, 120-132

Borsodi,N., Miskolczi,N., Angyal,A., Bartha,L., Kohan,J., Lengyel,A., (2011), Hydrocarbons obtained by pyrolysis of contaminated waste plastic , 45 th International Petroleum Conference, June 13, 2011, Bratislava, Slovak Republic, Catalyst

Jambeck, J.R, Roland Geyer, Chris Wilcox, Theodore R. Siegler, Miriam Perryman, Anthony Andrady, Ramani Narayan, dan Kara Lavender Law. (2015).Plastic Waste Inputs From Land Into The Ocean. Science. 3 February 2015 . Vol 347 Issue 6223.

Khan, N. S. M. and Kaneesamkandi, (2013), Biodegradable waste to biogas: Renewable Energy Source for the Kingdom of Saudi Arabia, *International Journal of Innovation and Application*, 4(1), 101-113

Krimadi L. (2013). Peningkatan Skala Proses Cracking Limbah Plastik Polipropilena Berkatalis Zeolit Alam Menghasilkan Bahan Bakar Minyak. Fakultas Matematika dan Ilmu Pengetahuan Alam. Universitas Cenderawasih. Jayapura.

Lestari, T. A. (2014). Studi Cracking Limbah Plastik High Density Polyethylene (HDPE) dengan Katalis Zeolit Alam. Fakultas Matematika dan Ilmu Pengetahuan Alam Universitas Cenderawasih, Jayapura.

Meidy S.A. (2016). Perengkahan (cracking) Lanjutan Produk Cair Pirolisis dengan Zeolit Alam Pada Proses Produksi Bensin Dari Sampah Plastik Polipropilen.. Fakultas Matematika dan Ilmu Pengetahuan Alam. Universitas Cenderawasih. Jayapura.

Mudasir, Karelius, Aprilita, N.H., and Wahyuni, E.T., (2018), Adsorption of mercury(II) on dithizone-immobilized natural zeolite, *Journal of Environmental Chemical Engineering*, 4(2), 1429-1439

Sadaf, S.N., Iqbal, J., Ullah, I., Bhatti, H.N., Nouren, S., Rehman, H., Nisar, J., and Iqbal, M., 2018, Biodiesel production from waste cooking oil: An efficient technique to convert waste into biodiesel, Sustainable Cities and Society, 41, 220-226

Sriningsih,W., Saerodji,M.G., Trisunaryanti,W., Triyono, Armunanto, R. and Falah,I.I., (2014), Fuel Production fraom LDPE Plastic Waste over Natural Zeolite Supported Ni, Ni-Mo, Co and Co-Mo Metals, *Procedia Environmental Sciences*, 20, 215-224

Wasini, E. (2019). Karakterisasi BBM hasil Pengolahan Limbah Plastik Tutup Galon Dalam Skala Pengolahan 50 Kg Di Pabrik Pengolahan Limbah Plastik. Jurusan Kimia FMIPA UCEN. Fakultas Matematika dan Ilmu Pengetahuan Alam Universitas Cenderawasih, Jayapura.