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The Characterization of Synthetic Zeolite for Hydrocracking of Waste Cooking Oil into Fuel

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Abstract

Zeolite A was used as hydrocracking catalyst to convert cooking oil into potential renewable fuels. The experiment was performed by characterize the diffraction, and pore properties the synthetic zeolite and it was confirmed the synthetic zeolite was zeolite A. The hydrocracking process of waste cooking oil was carried out in semi-fixed batch reactor system at 450° C for 2 hours, under the hydrogen flow of 20 ml/minute. The diffractogram and Si/Al ratio, 1.6, were matched to zeolite A properties, with the surface area, pore diameter, and pore volume were, 1.163 m^2/g, 3.93 nm, and 0.001 cc/g, respectively. Liquid product from hydrocracking process of cooking oil consisted of 28.99% alkane and alkene 26.59% that are potential as renewable fuels.

Keywords: *waste cooking oil; zeolite A; hydrocracking*

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INTRODUCTION

The production of cooking oil is continuously every year in which large countries in the world continue to produce waste cooking oil sourced from cooking oil derived from these plants, especially from CPO (crude palm oil). The accumulation of waste cooking oil is really high production. (Li et al., 2018) reported that America produce waste oil of 10 million tons/year, while China produce waste cooking oil of 5 million tons/year. From waste cooking oil are usually converted into oil equivalent to fossil fuels with various chemical processes. For example: transesterification, pyrolysis, and so on. From this process, waste cooking oil usually produces fuel oil products with poor conversion, therefore catalyst technology is used to improve the quality of product. At present, it is known that a suitable catalyst is zeolite synthesis (Khalife et al., 2017).

Zeolite is a material that has been widely used by various companies in the product purification process, especially in the petroleum field. Zeolites are widely used for adsorbents, ion exchangers, and heterogeneous catalysts in various applications. According to (Zheng et al., 2018) The advantages of zeolite as a catalyst are abundantly surface acidity, large surface area, excellent hydrothermal stability, and specific molecular separation ability (Zheng et al., 2018).

This research was characterized the zeolite synthesis and also testing the activity of refined cooking oil and waste cooking oil cracking. This catalytic process has also been known to be able to crack cooking waste oil into a fuel equivalent to fossil fuels. Most scientists have used cheap zeolite material but with high product efficiency, even close to the quality of fossil fuels (Kim et al., 2014). Zeolite is a relatively inexpensive catalyst and can be used repeatedly with a refining process, but with that, a simple zeolite catalyst has a pore size that is not too large, so that there is a limitation of function when there is a saturation. The development of catalysts currently uses synthetic catalysts instead of conventional zeolite catalysts.

Currently, several studies have been conducted on the use of synthetic zeolite catalysts to convert waste cooking oil to renewable fuels which are more useful. Li et al. (2015) was investigated on the conversion of waste cooking oil into jet fuel by using three types of zeolites (Meso-Y, SAPO-34, and HY) which are synthesized with nickel to convert waste cooking oil into biofuel for jet fuel. Mesoporous Zeolite Y shows the alkane selectivity with high jet fuel quality of 53% as well as the aromatic hydrocarbon selectivity of the jet range obtained is 13.4%. The developing of biodiesel from waste cooking waste oil was reported by (Romero-Izquierdo et al. 2019) that the biodiesel was obtained from esterification and transesterification with ethanol. The aviation fuel produced from hydro-process has been reported by (Chen and Wang 2019). One of the effects in the hydrocracking from waste cooking oil is temperature (Bezergianni et al. 2010; Zhang et al. 2014). This result is in the range of existing liquid fuel products.

MATERIALS AND METHODS

Materials

The experiment materials in this work was included the synthetic zeolite from Sigma Aldrich, H_2 Gas and waste cooking oil from restaurants around campus 3 of Universitas Ahmad Dahlan, Yogyakarta.

The experiment devices in this study consist of 1 unit of glassware, desiccator. Oven (Memmert Germany). The characterization Instrument by using *Atomic Absorption Spectrometer* (AAS, PERKIN ELMER 3110). Surface area analyzer *Gas Sorption Analyzer* (GSA, NOVA 2000, Quantachrome) was used determine the surface area parameters (surface area, pore volume and pore diameter) of the zeolite synthesis. The determination was based on physical adsorption of N_2 gas at batch temperature of 77.3K. XRD Expert Pro P Analytical for determination crystallinity of zeolite, spectrometer *Fourier Transform Infrared* (FTIR, Shimadzu Prestige-21). The FTIR analysis was used for testing the functional group content in the waste cooking oil. Catalytic activity of zeolite was evaluated in hydrocracking waste cooking oil by reactor shows in figure 1. The Liquid produce by Hydrocracking of waste oil was analyzed by *Gas Chromatography-Mass Spectrometer* (GC-MS, Shimadzu QP2010S).

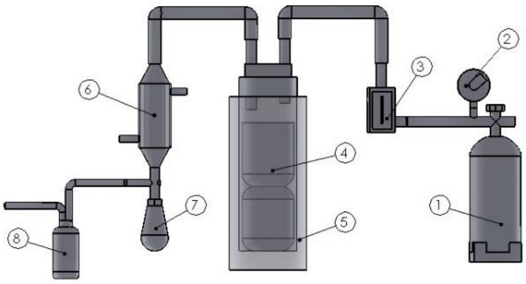

Figure 1. Experiment equipment of hydrocracking Oil and Refining

Where:

1. H_2 Gas
2. Pressure gauge
3. Gas Flow meter
4. Catalyst
5. Reactor
6. Reflux cooler
7. Storage
8. Accumulator

Research Procedures

The waste cooking oil was heated at temperature of 100-120°C to evaporate water then filtered with filter paper to separate the oil with large solid impurities. The liquid oil layer is separated again by a separating funnel. This Oil analysis with FTIR.

Analysis ratio Si/Al zeolite synthesis

The ratio of Si/AL of the zeolite was analyzed using Atomic Absorption Spectroscopy. The zeolite was destructed by dissolving it in hydrofluoric acid and aqua regia solution. Exactly of 10 mg of zeolite were dissolved in 1 mL of HF 40% and 1.5 mL Aqua regia solution. The aqua regia solution was made by mixing 1 mL HNO_3 65% and 3 mL HCl 37%. The dissolved zeolite then analyzed using AAS to check the Si/Al ratio content.

Crystallinity determination

The Christianity profile of the zeolite were characterized using X-Ray Diffractometer (XRD) in Material and Metallurgical Engineering laboratory ITS Surabaya.

Hydrocracking Process of Waste Cooking Oil

Exactly of 0.2 grams of zeolite was put into the catalyst container, 10 grams of waste cooking oil was put into the oil container, and the oil sample and zeolite were put into a hydrocracking reactor, as shown in Fig. 1. The reactor was installed with temperature of 450 °C for 2 hours with a flow of hydrogen gas 20 ml/min. The resulting of hydrocracking products was analyzed by GC-MS.

RESULTS AND DISCUSSIONS

Characterization of synthetic zeolite

The result Characterization of synthetic zeolite in Table 1.

Table 1. Zeolite catalyst characteristic test results

Characteristic	Value
Si/Al ratio	1.6
Specific surface area, m^2/g	1.16
Total pore volume, cm^3/g	0.001
Average pore diameter, nm	3.92

From table 1 that ratio of Aluminum (Al) and Silica (Si) were greatly affected the quality of zeolites as catalysts. The result shown that ratio of Si/Al was 1.6. This ratio was large enough to indicate Si in zeolite content. According to Norrozir the Si/Al ratio for zeolite A is 1-1.7 while the zeolite is HY 4.9. According Khalid et al. (2019) has investigated that the Si/Al ratio of zeolites are an important factor influencing thermal stability and hydrothermal stability, concentration and strength of Bronsted acid sites, and catalyst activity and selectivity.

The relatively high ratio of the Si/Al for zeolite A, which means there are more silica than the aluminum content, causes a decrease in the number of acid sites in zeolites. In general, zeolites with lower aluminum concentrations have higher levels of thermal and chemical stability. This result indicated that the zeolite would be good when used as an acid catalyst in the process of fluid catalytic cracking.

The zeolite porosity characteristics were included surface area, pore volume, and pore diameter. This pore characterization aims to determine the pore characteristics and capabilities that will be used for zeolite applications. Zeolite has been given base treatment to determine the pore distribution of the zeolite. Characterization with GSA is done by adsorption and desorption of N_2 gas on the zeolite surface. Calculations are done by Branauer – Emmett−Teller (BET) theory. The BET theory explains the phenomenon of adsorption of gas molecules to the surface of solids. N_2 gas is the most of gas that often used in pore character analysis using the BET theory. Table 1 shows the zeolite characterization in this study was carried out at a temperature of 77.35 K which is the boiling point of N_2. Data on specific surface area, total pore volume and mean catalyst pore network.

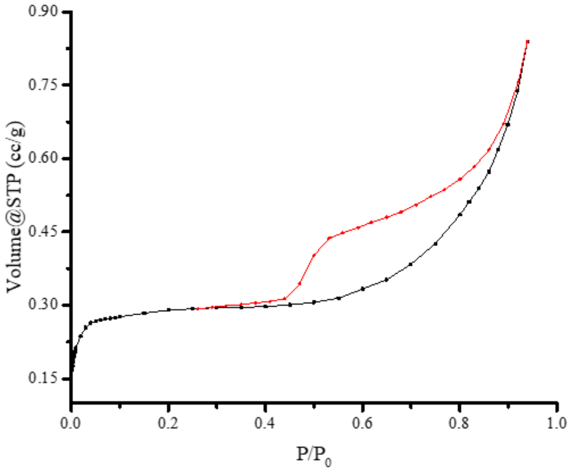

Figure 2. Isotherm graphic of the zeolite sample

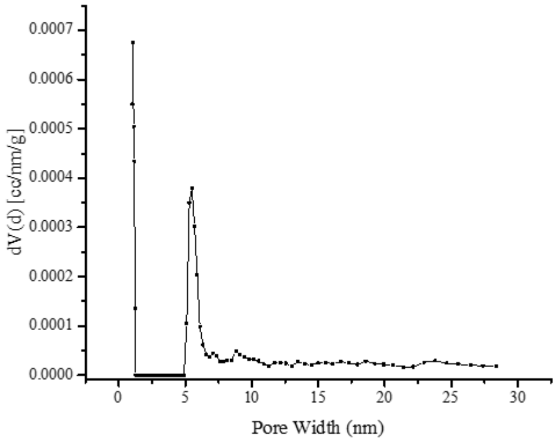

Figure 3. Pore size distribution of the zeolite sample

The zeolite sample have relatively large average pore diameter, 3.92 nm, which shown to be mesoporous materials. Although the sample has relatively large average pore diameter, the specific surface area and total pore volume was very low. This could be caused by the low porosity of the materials, despite it has high average pore diameter. The number of pores could be very low.

Isotherm of the zeolite sample is shown in Figure 2. In general, the sample has type IV isotherm with H3 hysteresis loop. This phenomenon indicating that the zeolite sample has wide range of pores size, and this hysteresis loop also known for having plate-like particles with slit shaped pores (Chu et. al. 2019). The wide range of pore size interpreted from isotherm curve is confirmed by the pore size distribution of zeolite sample, as shown in Figure 3. The zeolite has micropores at 1.061 nm and wide range of mesopores with the peak at 5.499 nm.

The porosity properties, especially specific surface area of the sample has indirectly affected the ability of the sample adsorption to reactants in hydrocracking.

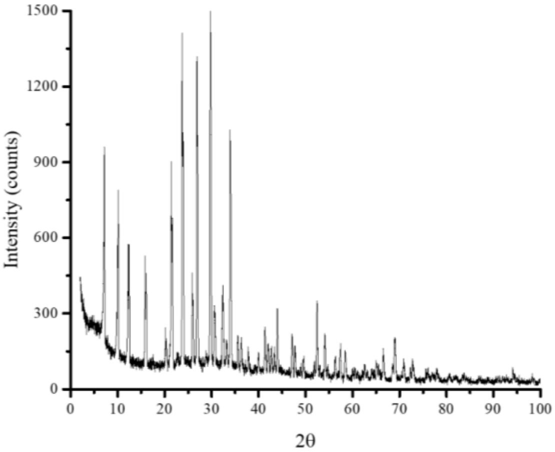

Figure 4. Diffractogram of zeolite samples.

According to Ferdov (2019) has investigated that the increase of adsorption on the catalyst surface, the possibility of product formation which is expressed as total conversion and activity of a catalyst will increase. The zeolite pore size greatly influences its activity as a catalyst, especially in petroleum processing. The micropore structure of zeolites causes hydrocarbon molecules with long carbon chains to not be diffused into their pores. This results in a fairly low percent conversion of catalytic cracking with zeolite. In the development of the world petroleum processing industry, cracking of hydrocarbon molecules with long chains is becoming increasingly important. This is due to the depletion of world oil reserves. Micropore size can cause a decrease in the activity and age of the zeolite Y catalyst due to the inhibition of the diffusion of large molecules (Groen et.al., 2007).

Figure 4 shows the three peaks of XRD. X-ray diffraction (XRD) measurements were performed to identify the crystallinity of the sample the measurement results show that the zeolite sample is a crystal. The diffractogram produced by Shimadzu 6000 X-ray diffraction produces the three strongest peaks. The synthetic zeolite was identified using software by comparing the detected XRD patterns with the standard pattern from the powder diffraction file data base supply the International Center for Diffraction Data (ICDD). Diffractogram of sample showed to be zeolite A, matched to the reference of ICDD 00-038-0241.

Based on the Si/Al ratio, pore properties and diffractogram data, it was confirmed that the zeolite sample was zeolite A with the average pore diameter of 3.92 nm, but has low porosity, which was shown by their low surface area and total pore volume.

Analysis of waste cooking oil with FTIR

The functional group content in waste cooking oil was analyzed by Fourier-Transform Infrared Spectroscopy (FTIR) instruments. The results are in Figure 5.

The FTIR spectra in figures 5 shows the absorption of the wavelength of intensity 1165 cm^{-1}, which shows the presence of carbonyl groups, absorption at (lambda symbol/wavelength) 1458.18 cm^{-1} indicates the presence of a methylene group (-CH_2-), uptake on 1743.65 cm^{-1} shows the presence of ketone groups, or aldehydes, uptake on 2924.09 cm^{-1} shows the CH absorption group on 3425.58 cm^{-1} shows the presence of OH groups.

Some functional groups that appear showing pure waste cooking oil and reflux waste cooking oil qualitatively show ester compounds. This is probably because the catalyst used in this process is limited to micropores. This is supported by research Cai et al. (2018). In his research on the pyrolysis of rice husks with the help of ZSM-5 catalyst with micro-sized pores. The results obtained are mostly esters and phenols.

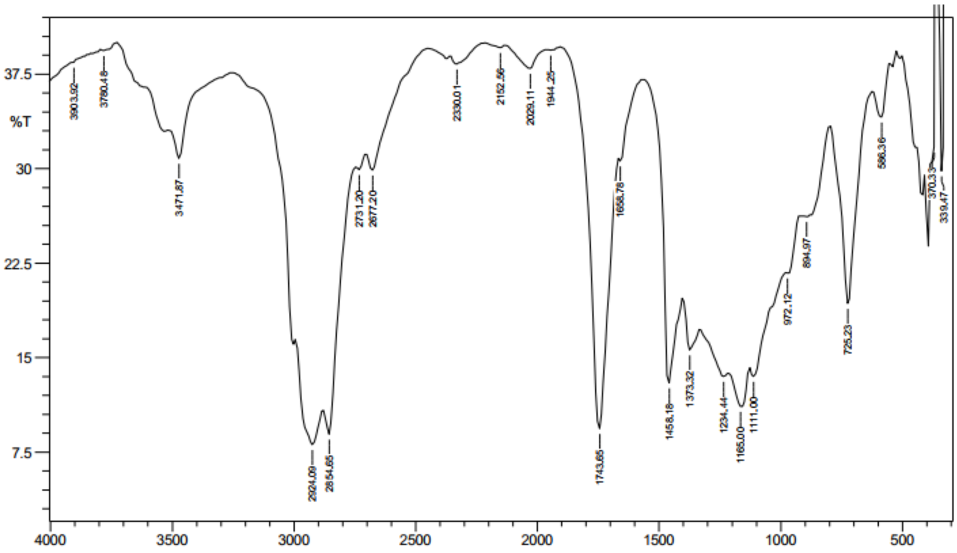

Figure 5 Analysis of waste cooking oil with FTIR

Hydrocracking of Waste Cooking Oil

The results of the GC-MS analysis of waste cooking oil shown in Figure 6. The compounds found in GCMS were ester, which is the consequence of the esterification step prior to GCMS analysis and interpreted as its free fatty acid form.

The waste cooking oil mainly consist of 6 compounds, as shown in Table 2. Petroselinic and palmitic acid were the biggest constituent of waste cooking oil and would be converted into shorter chain of hydrocarbon.

Table 2. Composition of waste cooking oil from MS

Free Fatty Acid	Lipid Numbers	Composition %
Myristic acid	C14:0	7.36
Palmitic acid	C16:0	33.46
Petroselinic acid	C18:1	50.25
Stearic acid	C18:0	3.08
Oleic acid	C18:1	2.6
Linoleic acid	C18:2	2.81

Anand et. al. (2016) explained that the conversion of vegetable oils, which consist of triglyceride and free fatty acid, could undergoes oxygen removal reactions, such as depropanation of triglyceride, decarboxylation, decarboxylation, and hydrodeoxygenation of free fatty acid.

From Figure 7, the hydrocracking product with zeolite A catalyst contains 67 compounds which are grouped into 6 groups of compounds based on their functional groups, namely alkane, alkene, aldehyde, alcohol, ketone and carboxylic acid. The wide range of product shown in Figure 8 also indicating the selectivity of zeolite A towards hydrocracking of waste cooking oil at mentioned reaction condition. Although the spread was relatively high, the most dominant hydrocarbon product was undecane ($C_{11}H_{24}$) with the percentage of 5.25%.

In this research, zeolite A catalyst can cracked triglyceride and free fatty from waste cooking oil, into fuel, as shown in Figure 8. Alkane and alkene products were very potential to be used as fuel because of their similarity with conventional petroleum fuel, which is consist of carbon and hydrogen only, or hydrocarbon. The presence of hydrocarbon, 28.69% alkane and 26.59% alkene, in the hydrocracking product indicating that oxygen removing reaction has occurred in the catalytic hydrocracking system.

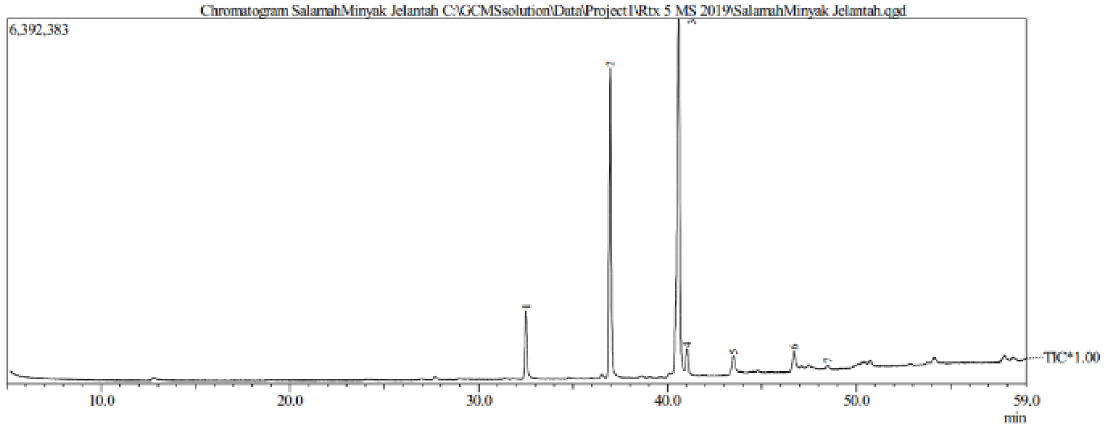

Figure 6. Chromatogram of hydrocracking waste cooking oil

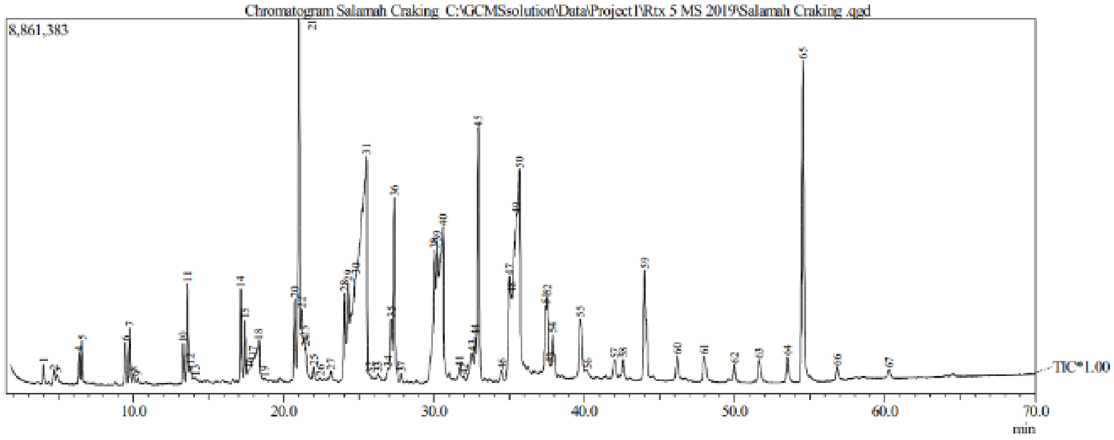

Figure 7. Chromatogram of waste cooking oil hydrocracking with zeolite A catalyst

However, there were significant amount of percentage on non-hydrocarbon product, 41.22% carboxylic acid, which ranged from short carbon chain, to the longer chain. The high percentage of carboxylic acid that ranged in shorter to longer chain of carbon, indicating that C-C scission still could occurred using zeolite A, but the oxygen removal reactions only happened in relatively small proportions, but still very potential to produce hydrocarbon as renewable fuels.

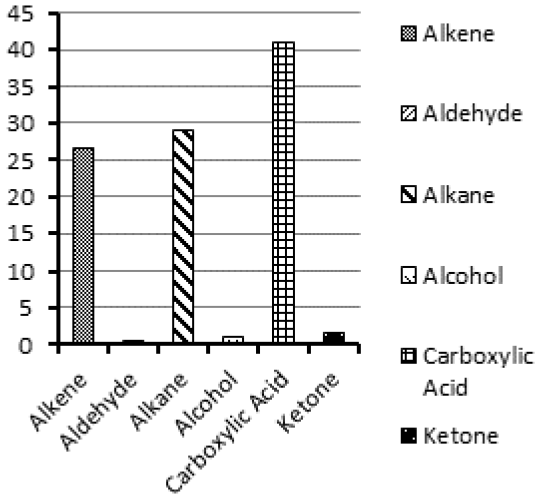

Figure 8. The content of waste cooking oil hydrocracking compound with zeolite A catalyst

CONCLUSION

The zeolite sample has a Si/Al ratio: 1.6. The zeolite sample has specific surface area characteristics of 1.163 m/gr, average pore diameter of 3.92 nm and volume of 0.001 cc/g. The zeolite sample was obtained zeolite A. Zeolite A can be used for waste cooking oil hydrocracking by producing hydrocarbons of as much as 28.99% alkane and 26.59% alkene.

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