Catalytic cracking of polyethylene terephthalate (PET) plastic waste and palm fibre mixtures using Ni-USY zeolite catalyst

Nazarudin1,2*, N Jayanti1, O Alfernando1, I G Prabasari1, Uylarti3 and R Sarip4
1 Chemistry Engineering Study Program, Faculty of Engineering, Universitas Jambi, Indonesia
2 Center of Energy and Nanomaterial Study, Universitas Jambi, Indonesia
3 Agricultural Product Technology Study Program, Faculty of Agricultural Technology, Universitas Jambi, Indonesia
4 Chemistry Department, Faculty of Science, University of Malaya, Malaysia

*Corresponding author: nazarudin@unja.ac.id

Abstract. This research was carried out to produce fuel (Oil Liquid Product/OLP) from catalytic cracking of a mixture of Polyethylene Terephthalate (PET) and fiber waste from palm oil. USY zeolite was previously ion-exchanged by three levels of Ni-metal concentration (1%, 2%, 3%) before used as catalyst in the cacking process. The catalytic cracking was carried out at ratio of sample to catalyst was 6:1, three levels of temperature (400°C, 425°C and 450°C) and three levels of reaction time (10, 20 and 30 minutes). The SEM images and EDX spectra of Ni-USY zeolite catalysts showed that all catalysts were in crystalline form of FAU framework. The highest of OLP percentage, 24.5%, was produced by catalytic cracking at 450°C for 10 minutes using Ni-USY prepared by ion-exchange using 2% concentration of Nickel Nitrate solution.

1. Introduction
The increase need for plastic may lead to the increase of plastic waste and environmental problem. In Indonesia, the average need for plastic is 200 ton per year. Polyethylene Terephthalate (PET) is the most type of plastic produced. Polyethylene terephthalate (PET) can be used to produce disposable bottle drink [1]. One route of eliminating environmental pollution from plastic waste is by recycling. Chemically, plastic recycling can be processed by thermal or catalytic cracking [2-8].

Catalytic cracking is more effective than thermal cracking due to low energy activation leading to lower temperature and shorter time of reaction [9]. There are any catalyst that can be used for plastic cracking such as ZSM-5, MCM-41 and USY (Ultra-Stable Y zeolite) [2, 6, 10]. Mixing substrate is known to lower activation energy of catalytic cracking reaction. Catalytic cracking mixture of plastic and biomass at 250-500°C produced fuels C10+ and aromatic compound [11, 12]. The activation energy for this catalytic cracking was lower (173.27 kJ) compare to activation energy for biomass alone (185.87 kJ/mol) and plastic alone (249.87 kJ/mol).

Plastic cracking using USY catalyst without embedded metal produced liquid fuel with low conversion [13]. Embedding metal such as Ni to catalyst is known to increase cracking conversion. Ni is frequently used because it forms weak bond with reactants, therefore product is easily separated from catalyst surface [14]. There are several methods have been developed to embed Ni to catalyst, one of them is by ion exchange. This research aimed to produce Ni-USY catalyst and to investigate its
performance on the catalytic cracking of Polyethylene Terephthalate (PET) plastic waste and palm fiber mixtures to produce alternative fuels.

2. Material and Methods

2.1. Materials and Sample preparation
PET (Polyethylene Terephthalate) plastic waste was provided by Bank Sampah Bangkitku Kota Jambi, Palm Fiber was provided by PT Sumbertama Nusa Pertiwi, N₂ and O₂ were provided by PT Rezeki Suya Gasindo, H-USY and Ni(NO₃)₂·9H₂O were from Sigma Aldrich. The instruments used were semi batch cracking reactor, calcination reactor, and cylinder furnace. PET plastic waste was cut into small pieces 2 mm x 2mm using counter machine at Bank Sampah Bangkitku, Kotabaru, Jambi. The pieces were further washed and air dried. Palm fibre were cut using scissors to 2 mm before used in the cracking.

2.2. Catalyst preparation and catalyst characterisation
NH₄⁺-USY was placed in glass reactor for calcination process. The calcination was carried out by flowing O₂ gas to the reactor at 550°C for 5 hours. The product was H-USY. Before Ni embed was carried out, Ni-Nitrate solutions (Ni(NO₃)₂·9H₂O) 1%, 2%, dan 3% were prepared. The 3% Ni-nitrate solution was first made by dissolving 44.1176 g Ni(NO₃)₂·9H₂O to 250 ml solutions using distilled water. The 1 and 2% Ni-nitrate solution were prepared by dilution of 3% Ni-nitrate solution.

Ni-embed was carried out by ion exchange as follow: H-USY catalyst was mixed in Ni-Nitrate solution (1%, 2%, and 3%) at ratio 1:10. This mixtures were mixed for 24 hours at room temperature. The mixtures were filtered and rewashed using distilled water until pH for waste water reached 7. The solid filtered in the filtered paper was furthered dried using oven drier at 105°C for 24 hours. The solid was furthered underwent calcination at 550°C for 5 hours with oxygen flow in the reactor.

2.3. Catalysts were characterised using SEM, SEM-EDX and XRD.

2.3.1. Catalytic cracking and analysis of cracking products
The mixture of PET plastic waste and palm fibre (1:3 by weigh) were placed in the reactor along with Ni-USY catalyst with ratio catalyst to sample 1:6. The samples were cracked at different temperatures: 400°C, 425°C, 450°C and different time: 10, 20 and 30 minutes. Percent conversion for each cracking product, total conversion, and conversion ratio were calculated using equation used by Nazarudin [5] as shown below:

\[
\text{\% cracking product} = \left( \frac{\text{weight of cracking product}}{\text{initial weight of feed}} \right) \times 100 \% \\
\text{\% total conversion} = \left( 1 - \frac{\text{weight of residue}}{\text{initial weight of feed}} \right) \times 100 \% \\
\text{Selectivity} = \left( \frac{\text{gas conversion} + \text{oil liquid conversion}}{\text{coccas conversion}} \right)
\]

3. Result and Discussion

3.1. Catalyst Characterization
The elements in the catalyst as determined using SEM EDX are presented in Table 1. The ratio Si/Al in H-USY is 2.96. Previously there was Na at H-USY which later on was exchanged with Ni during catalyst modification by ion exchange using several concentrations of Ni-Nitrate solution.
Table 1. Metal concentration in H-USY as shown by SEM EDX

| Element | Content (%) |
|---------|-------------|
| Si      | 69.98       |
| Al      | 23.63       |
| Na      | 6.40        |

Figure 1. XRD diffraction patterns of H-USY (a); H-USY ion exchanged using Ni-Nitrate 1% (b); H-USY ion exchanged using Ni-Nitrate 2% (c); H-USY ion exchanged using Ni-Nitrate 3% (d)

Figure 2. SEM Image of: H-USY (a); H-USY ion exchanged using Ni-Nitrate 1% (b); H-USY ion exchanged using Ni-Nitrate 2% (c); H-USY ion exchanged using Ni-Nitrate 3% (d)

XRD patterns for H-USY and Ni-USY catalysts are presented in Figure 1. The highest peak intensities shown in Figure 1 match to peaks of H-USY with FAU structure and denotes highest intensity at angle $2\theta = 6.2^\circ; 15.6^\circ; 20.4^\circ; 23.6^\circ; 27^\circ$; and $31.3^\circ$ [15-19]. Therefore, it can be concluded that all catalyst diffraction patterns correspond to standard and count for FAU, although the peak
intensities at angle 2θ = 6.2°; 15.6°; 20.4°; 23.6; 27; and 31.3 showed small differences among different concentrations and as well as from H-USY. This may due to metal deposits in the catalyst samples which cover up pores surfaces. The decrease in catalyst peak may be caused by the lost of some structural cation leading to the decrease in catalyst persistence and collapse in catalyst structure [7,18-19]. Ion exchange of H-USY zeolite catalyst using Ni-nitrate solution did not change their morphology as seen by SEM images (Figure 2).

3.2. Thermal cracking
The highest oil liquid product was produced by cracking at 450°C. The oil liquid products at 10, 20 and 30 minutes of cracking were 17%, 14.33% and 15.67% respectively. The increase in temperature increased the amount of oil liquid product. Condensation process also affected the production of oil liquid.

The condensation process affect how much oil liquid was collected. The higher the temperature increased the amount of gas produced, however, if condensation temperature is as low as temperature for gas condensation, there will be more gas being condensed and produces oil liquid product. At the lowest cracking temperature (400°C), the process was able to produce oil liquid product eventhough there was no catalyst was presented. This condition was used for our next experiment using catalyst.

3.3. Catalytic cracking
Oil liquid product from catalytic cracking of PTE plastic waste and palm fibre mixtures was obtained at 10 minutes reaction. There was no oil liquid product obtained at 20 and 30 minutes reaction. Oil liquid was brownish yellow and was not frozen at 15°C. As shown in Table 2, the highest percentage of oil liquid product of cracking using Ni-USY 1% was obtained at 450°C and the lowest was cracking at 425°C. Percentage of gas product was inversely proportional to oil liquid product, in which the highest oil gas product was obtained at 425°C and the lowest was obtained at 450°C. This may be due to unstable nitrogen flow, that the higher nitrogen flow may take some product out before being condensed. At catalytic cracking using Ni-USY 2% and 3%, the increase in temperature increased the amount of oil liquid product and decreased the amount of oil gas products. The highest coccas (32.67%), was produced at 450°C using Ni-USY 2%. However, during catalytic cracking using Ni-USY 3%, the highest coccas produced (24.83%) was at temperature 425°C.

| No. | Ni-Nitrate concentration | Temperature (°C) | Oil Liquid (%) | Oil Gas (%) | Coccas (%) |
|-----|--------------------------|------------------|----------------|-------------|------------|
| 1.  | 1%                       | 400              | 15.50          | 61.83       | 22.67      |
| 2.  | 1%                       | 425              | 14.00          | 64.67       | 21.33      |
| 3.  | 1%                       | 450              | 20.67          | 57.67       | 21.67      |
| 4.  | 2%                       | 400              | 14.00          | 66.00       | 20.00      |
| 5.  | 2%                       | 425              | 22.00          | 58.33       | 19.17      |
| 6.  | 2%                       | 450              | 24.50          | 43.67       | 32.67      |
| 7.  | 3%                       | 400              | 18.50          | 57.67       | 23.83      |
| 8.  | 3%                       | 425              | 21.33          | 53.83       | 24.83      |
| 9.  | 3%                       | 450              | 24.83          | 51.67       | 23.50      |

3.4. Cracking product selectivity
Product selectivity from thermal and catalytic cracking using H-USY and Ni-USY are presented at Figure 3 and 4. Although gas conversion was high during thermal cracking, the selectivity was the lowest among other cracking. As seen in Figure 3, the use of catalyst could increase ratio oil liquid conversion to oil gas conversion.
Figure 3. Ratio of oil liquid conversion to oil gas conversion at different cracking of PET and palm fibre mixture

Figure 4. Product selectivity for cracking of PET and palm fibre mixtures

Table 3. Products of catalytic cracking of PTE plastic waste and palm fibre mixtures using H-USY and Ni-USY 2%

| No. | Reaction time (minutes) | Temp (°C) | Oil liquid (%) | Oil Gas (%) | Coke (%) |
|-----|------------------------|-----------|----------------|-------------|----------|
|     |                        |           | H-USY          | Ni-USY      | H-USY    | Ni-USY | H-USY | Ni-USY |
| 1.  | 4                      | 400       | 9.33           | 14.00       | 47.67    | 67.67  | 43.00 | 18.33  |
| 2.  | 4                      | 425       | 10.17          | 16.00       | 44.00    | 52.67  | 45.83 | 31.33  |
| 3.  | 4                      | 450       | 8.33           | 14.83       | 43.67    | 64.00  | 48.00 | 21.17  |
| 4.  | 7                      | 400       | 10.17          | 14.17       | 49.33    | 67.67  | 40.50 | 18.17  |
| 5.  | 7                      | 425       | 13.50          | 16.67       | 41.00    | 57.83  | 45.50 | 25.50  |
| 6.  | 7                      | 450       | 12.33          | 19.50       | 50.00    | 54.50  | 37.67 | 26.00  |
| 7.  | 10                     | 400       | 11.33          | 14.50       | 52.50    | 63.33  | 36.17 | 22.17  |
| 8.  | 10                     | 425       | 14.33          | 22.00       | 43.00    | 61.33  | 42.67 | 16.67  |
| 9.  | 10                     | 450       | 14.67          | 24.50       | 41.33    | 59.17  | 44.00 | 16.33  |
3.5. Catalytic cracking using H-USY and Ni-USY 2%
Catalytic cracking of PET and palm fibre mixture was carried out using H-USY and the chosen Ni-USY catalyst. Ni-USY was chosen according to its performance during catalytic cracking of PET and palm fibre mixture: the highest oil liquid product, stable increase in oil liquid production and the most flammable. The catalyst which fulfil this criteria was Ni-USY 2%. The catalytic cracking using Ni-USY 2% was carried out using ratio catalyst to sample 1:6, temperature 400°C, 425°C, 450°C and reaction time 4, 7, and 10 minutes. Detail product of this cracking is presented at Table 3. It can be seen that oil liquid product was increased with time. Modification of catalyst H-USY using Ni-nitrate 2% was proved can increase oil liquid and oil gas product and decrease coccas production.

4. Conclusion
The current research was successfully synthesize Ni-USY catalyst which can be applied for cracking of PET plastic waste and palm fibre mixtures to produce alternative fuels. Ni-USY has FAU structure. The cracking of PET plastic waste and palm fibre mixtures at 450°C for 10 minutes using Ni-USY synthesized using 2% Ni-nitrate generated the highest oil liquid product (24.5%).

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References
[1] H. P. Austin, M. D. Allena, B. S. Donohoe, N. A. Rorrer, F. L. Kearnsd, R. L. Silveira, B. C. Pollard, G. Dominick, R. Duman, K. E. Omarif, V. Mykhaylyk, A. Wagner, W. E. Michener, A. Amore, M. S. Skaf, M. F. Crowley, A. W. Thorne, C. W. Johnson, H. L. Woodcock, J. E. McGeehan and G. T. Beckham 2018 Proceedings of the National Academy of Sciences of the United States of America (National Academy of Sciences), Vol. 115, pp. 1-8
[2] Leonenko S V, Kudryavtsev S A and Glikina I M 2017 J. Adsorpt. Sci.&Technol. 35 (9-10) 878-873
[3] Lerici L C, Renzini M S and Pierella L B 2015 Procedia Mater. Sci. 8 297-303
[4] N. Miskolcz, T. Juzsakova and J. Soja 2019 Journal Of The Energy Institute 92 (1), 118-127
[5] Nazarudin 2012 Catalytic Cracking of Plastic Waste Using Nanoporous Materials (Doctor of Philosophy Thesis) University College London
[6] Persson H, Duman I, Wanga S, Petterssonb L J and Wanga J 2019 J. Anal. Appl. Pyrolysis 138 54-61
[7] Sarker S K and Hoque A H M S 2016 Int. J. of: Sci. Basic Appl. Res. 30(3):29-38
[8] Almeida D and Marques M D F 2016 Polimeros 26(1):44-51
[9] Ratnasari D K, Nahil M A and Williams P T 2017 J. Anal. Appl. Pyrolysis 124 631-637
[10] Y. Zheng, L. Tao, X. Yang, Yuanbo, Huang, C. Liu and Z. Zheng 2018 J. Anal. Appl. Pyrolysis 133, 185-197
[11] Miskolcz N, Bartha L and Angyal 2009 Energy Fuels 23 2743-2749
[12] Akpanudoh N S, Gobin K and Manos G 2005 J. Mol. Catal. A: Chem. 235(1-2):67-73
[13] Saha S, Sharma A, Purkayastha S, Pandey K and Dhingra S 2019 Plastics to Energy (New York: William Andrew Applied Science Publishers) pp. 365-376.
[14] Cerqueira H S, Ayrault P, Datka J and Guisnet M 2000 Microporous Mesoporous Mater. 38 197
[15] Chester A W and Derouane E G 2001 Zeolite Characterization and Catalysis (Heidelberg: Springer)
[16] Fecheteya I, Wangb Y and Védrine J C 2012 Catal. Today 189 2-27
[17] Rosmawati R, Arita S, Komariah L N, Nazarudin N, Alfernando O 2019 Indones. J. Fundam. Appl. Chem.4(2) 67-71
[18] Makorova M K and Dwyr J 1993 J. Phys. Chem. 97 6337-6338
[19] Gabrienko A A, Danilova I G, Arzumanov S S, Torktarev A V, Freude D and Stepanov A G 2010 Microporous Mesoporous Mater. 131 210–216