CATALYTIC PYROLYSIS OF POLYPROPYLENE PLASTIC FROM MUNICIPAL SOLID WASTES INTO GASOLINE FRACTION COMPOUNDS USING THE MIXED NICKEL (Ni) AND CHROME (Cr) METALS AS THE CATALYST

KATALITIK PIROLISIS PLASTIK POLIPROPILENA DARI SAMPAH PADAT PERKOTAAN MENJADI SENYAWA FRAKSI BENSIN MENGGUNAKAN CAMPURAN LOGAM NIKEL (Ni) DAN KHROM (Cr) SEBAGAI KATALIS

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ABSTRAK

Pada dekade terakhir limbah plastik, yang berasal dari sampah padat perkotaan, telah diidentifikasi sebagai masalah lingkungan seluruh dunia. Daur ulang secara kimia adalah salah satu metode alternatif untuk mengatasi masalah tersebut. Limbah plastik polipropilena didegradasi secara termal dan katalitik dengan adanya zeolit alam dengan tambahan logam kromium (Cr) dan nikel (Ni) dalam suatu reaktor unggun-tetap pada kisaran suhu 400-500°C, untuk memperoleh bahan bakar cair yang tepat guna. Ketergantungan terhadap suhu proses, pengaruh katalis, pada perolehan fraksi bahan bakar ditentukan dan dibandingkan dengan fraksi bensin komersial. Diamati bahwa pada suhu 400-500°C, produk terbanyak dari degradasi (pirolisis) termal dan katalitik adalah fraksi cair (bensin) dan produk terbanyak yang diperoleh pada suhu 450°C (77,84%). Penggunaan logam khrom dan nikel pada zeolit alam teraktifasi sebagai katalis dua-fungsi dan meningkatkan perolehan fraksi cair dan keasaman katalis. Produk cair yang diperoleh dalam proses ini dianalisis dengan menggunakan GC untuk komposisinya. Katalis sintetis, zeolit alam teraktifasi dan zeolit alam dikarakterisasi dengan fisisorpsi nitrogen (BET), porositas, XRD, dan keasaman. Dari dasar produk yang dihasilkan, katalis yang mengandung khrom 6% dan nikel 4% pada zeolit alam teraktifasi sebagai katalis terbaik untuk proses degradasi (pirolisis) katalitik untuk memproduksi bahan bakar cair (bensin). Konversi katalitik menggunakan katalis tersebut dapat dipakai sebagi metode alternatif untuk mendaur ulang limbah plastik menjadi yang lebih bernilai dan minyak bahan bakar.

Kata Kunci: limbah plastik, sampah padat perkotaan, pirolisis, katalis, zeolit alam, khrom, nikel, fraksi bensin

ABSTRACT

Plastic wastes which come from municipal solid wastes, have been identified as the worldwide environmental problem in the last decades. Chemical recycling is one of the alternative methods to solve such problem. Inorder to obtai appropriate liquid fuels, polypropylene plastic waste was degraded thermally and catalytically in the presence of natural zeolite incorporated with chromium (Cr) and nickel (Ni) metals. The reaction was conducted in a fixed bed reactor in the temperature range of 400-500°C. The dependencies of process temperature and effect of catalyst on yield of the fuel fractions were determined and compared to commercial gasoline fractions. The current study shows that the major product of thermal degradation (pyrolysis) and catalytic degradation is liquid (gasoline) fraction and the highest products obtained at temperature 450°C is approximately 77.84%. The use of chromium and nickel metals on activated natural zeolite as a bi-functional catalyst enhance the yield of liquid fractions and the acidity of the catalysts. The *liquid product obtained in this process was analyzed using GC for its composition. Synthesized catalysts, activated natural zeolite and natural zeolite were characterized by means of nitrogen physisorption (BET), porosity, X-ray diffraction (XRD), and acidity. Based on the obtained results, the catalyst containing 6% of chromium and 4% of nickel on activated natural zeolite is a good catalyst for conversion of polypropylene plastic wastes to liquid (gasoline) fuels. Catalytic conversion using such catalysts may applicable as an alternative method for recycling plastic wastes to more valuable commodities such as fuel oils.*

Keywords*: plastic waste, municipal solid waste, pyrolysis, catalyst, natural zeolite, chromium, nickel, gasoline fraction*

I. INTRODUCTION

The shortage of petroleum resources, environmental pollution, energy security, and continuous increasing petroleum costs encourage new studies or researches to develop alternative fuel resources. Plastic wastes, which come from the municipal solid wastes, are one of the most promising resources for fuel production due to its high heat of combustion and because of the increasing availability in local communities. Plastics are an essential part of our modern lifestyle because of their excellent properties such as light weight, durability and energy efficiency and are utilized in almost all of our everyday activities (Panda et al. 2010, Plastics 2013, Singhabhandhu & Tezuka 2010). The enormous world population increase coupled with the improved living conditions of the people led to a dramatically increase of the consumption of plastics worldwide. Moreover, the consumption demand for plastic materials has steadily increased because of their flexible utilities, relatively low cost and durability when compare with other materials (Obah et al. 2009). Some of the most used plastics are polyolefins such as polyethylene and polypropylene, which have a huge production and consumption in many applications.

The world's annual plastic consumption increased dramatically from around 2 million tons in the 1950s to about 288 million tons in 2012 with a 15% increase yearly (Panda et al. 2010, Production 2012, UNEP 2009). In 2008, worldwide plastics production was around 245 million tons and global production of plastics reached 280 million tons in 2011 (Plastics 2013, Production 2012). In term of volume, polypropylene is the largest commodity plastic material in the world, the polyvinyl chloride is the second largest and the third-largest is the high-density polyethylene (HDPE) (Kumar et al. 2011, Plastics 2012, UNEP 2009). However, Indonesia plastics consumption around 1.9 million tons in first-semester 2013 (Industry Plastic http://kemenperin.go.ig). The Indonesian Olefin, Aromatic and Plastic Association (INAplas) reported that plastic consumption in Indonesia is still relatively low on a per-capita basis at just over 17 kilograms (kg) per year, compared to around 35 kg in Malaysia and Thailand and 40 kg in Singapore (Global 2014). Hence, plastic wastes are increasing rapidly and contribute extensively to the problem of waste management. Plastic wastes represent a large fraction of municipal solid waste.

Disposal of a large amount of plastic waste, as the municipal solid waste, has been identified as worldwide environmental problem in the last decades. Plastic wastes production in Indonesia are around 5.4 million tons per year or 14% of total waste generation (State Ministry 2008). A number of alternative methods have been tried to solve the problems of plastic waste from the municipal solid waste, such as land filling, incineration, bio- and photo-degradation. However, land filling or incineration method is facing great social refusal to accept because of environmental problems such as air pollution and soil contamination, as well as economical defiance due to the increase of space and disposal costs. Also these methods do not correspond to current environmental regulations. For example, landfill has environmental risks due to the plastic wastes do not biodegrade in landfills. Therefore, in the near future, a disposal of plastic waste in landfills will be almost impossible because of the law, high costs and growing ecological social awareness. Incineration is not extensively used primarily because of stimulates the growing emission of detrimental and greenhouse gases e.g. NOx, SOx, COx etc, which only alter a solid waste issue to an air pollution problem. The bio-and photo-degradation rates are too slow under normal conditions.

Therefore, to minimize the effect of resulted land filling and incineration that there is the need for better approach to resolve the treat without of necessity creating more problems. One of the alternative ways to overcome the abundance plastics waste problem and also to increase its economic value is by converting plastics waste into fuels using thermal degradation (pyrolysis) and catalytic degradation process. During the last decade, chemical recycling has been of great interest in terms of environment concerns and economic possibility, namely a conversion of plastic wastes into hydrocarbon feedstock or fuel oil for a variety of downstream processes (Panda 2010). From the waste-to-energy point of view plastic wastes have been considered good candidates of feedstocks for energy conversion because of their high heating values. There are three different methods to get fuel product from plastic waste, that is thermal degradation or pyrolysis, catalytic degradation, and gasification (Al-Salem et al. 2009, Al-Salem et al. 2010, Brems et al. 2013, Panda et al. 2010, UNEP 2009). When compared to the pyrolysis, the catalytic degradation (catalytic pyrolysis) is preferred to improve the yield of valuable products, lower the reaction temperature, high reaction rate and lower temperature of degradation and increase the yield of gasoline (C_5–C_{12}) or the chemical distribution of the product is narrower than in thermal process.

There are many of researchers and experts have done a lot of researchs and works on waste plastics; some their works based on thermal degradation process (Miskolezia et al. 2004, Panda 2010, Stelmachowski & Slowinski 2012) and catalytic degradation process (Aguado et al. 2007, Elordi et al 2011, Farsh et al 2013, Gaca et al. 2008, Huang 2010, Jan et al. 2010, Kaminsky & Zorriqueta 2007, Lin & Yang 2007, Lopez et al. 2011, Obah et al. 2009, Obah et al. 2011, Obah et al. 2012, Sarker & Rashid 2013, Sener 2006, Trisunaryanti et al. 2013, Wanchai & Chaisuwan 2013). The catalysts most frequently used in the catalytic degradation or pyrolysis-cracking are different types of zeolites (Hβ, HY, mordenite, HZSM-5) (Aguado et al. 2007, Farshia et al 2013, Lopez et al 2011, Trisunaryanti et al. 2013, Wanchai & Chaisuwan 2013), acid solids like alumina, silica alumina (Obah et al. 2009, Obah et al. 2011, Sarker & Rashid 2013), ordered mesoporous aluminosilicates (Al-MCM-41 and Al-SBA-15) (Gaca et al. 2008, Obah et al. 2012, Sener et al. 2006), Ziegler-Natta, (Kaminsky & Zorriqueta 2007), bentonite (Farshia et al. 2013), carbonate (Jan et al. 2010), and equilibrated FCC catalysts (Huang et al. 2010, Lin & Yang 2007). However, the use of catalyst is the main cost burden for recycling of plastic wastes by pyrolysis. Reducing the catalyst cost for small scale application in developing countries like Indonesia is very interesting challenges. Natural zeolites which can be found in many places worldwide including Indonesia might be used as a candidate for this purpose instead of the commercial catalysts.

The demand for polypropylene (PP) in the world is about 25 wt% of thermoplastic and is steadily increasing. Therefore, PP which is one of the largest parts of both industrial and domestic wastes, is selected to be a model of sample used in this study. The objective of this current study is to obtain the best catalyst applicable for the conversion of polypropylene plastic waste into fuel oils via pyrolysis and catalytic pyrolysis processes. In addition, the effect of introducing the chrome (Cr) and nickel (Ni) on natural zeolite as catalysts is also studied.

II. METHODOLOGY

A. Sample preparation

The waste plastic samples used in this experiment were obtained from local supermarkets and groceries. The samples were sorted, cleaned from contaminations using detergent, dried, and cut by using scissors manually prior to process in the reactor. The cutting sample size ranges from 14 mm–15 mm.

B. Catalyst Preparation

The catalysts used for these works were natural zeolite (ZA) and synthesized Ni-Cr on natural zeolite as support. Natural zeolite was obtained from PT. Bratako Serpong, Indonesia. Catalysts were prepared using a method of mixing, metals impregnation, drying and calcinations. Natural zeolite (ZA,100 mesh) was pre-treated, before impregnated with Ni and Cr metals, by adding HF 1% solution for 10 minutes then washed using distilled water, dried at 120^oC for 1 h. Then the dealumination of pretreated natural zeolite was conducted by reflux with HCl 3M at 80^oC for 1 hr and washed and dried at 120^oC for 2 hrs. Reflux treatment was repeated with NH_4Cl at 70^oC for 2 hrs, then washed and dried at 120^oC for 2 hrs. After dealumination, the treated natural zeolite was calcined at 500^oC for 5 h, produced the ZAA (treated natural zeolite) as catalyst and/or support samples.

Nickel and Chrome-natural zeolite composite was prepared by impregnating of treated natural zeolite (ZAA), with Ni-Cr metal pair solution of nickel nitrate hexahydrate [$Ni(NO_3)_2.6H_2O$] and a solution of chromium nitrate enneahydrate [$Cr(NO_3)_3$ $9H_2O$]. The nickel content on catalyst was 4%-wt and chromium content was varied from 4 to 8%-wt (4, 6, and 8%) to produced catalyst NiCr4-ZAA (catalyst A), NiCr6-ZAA (catalyst B), and NiCr8-ZAA (catalyst C), respectively. After impregnation at 70-80°C for 3 hrs, then dried at 120°C for 2 hrs and calcined at 500°C for 5 hrs.

The catalysts were characterized for surface area, porosity and acidity. The BET surface area, pore volume and pore size distribution were obtained from nitrogen adsorption desorption isotherms measured at 77K by a Quantachrome, NOVA 1200 porosimeter, using the BET method. The total acidity was determined in the temperature range 180 to 800°C by ammonia adsorption-desorption method.

C. Thermal Gravimetric Analysis (TGA)

The sample is pre-analyzed using Thermogravemetric analyzer (TGA). The thermal degradation temperature of plastic waste was measured using the Setaram TA824 instrument. A typical TGA instrument consists of a precision mass balance which records the initial and instantaneous mass of a sample and a furnace to increases the

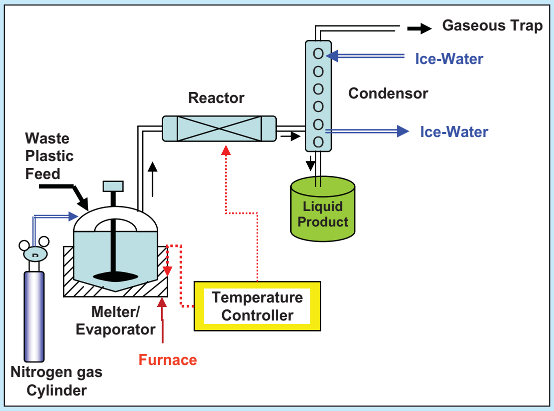

Figure 1
Scheme of thermal and catalytic pyrolysis of plastic waste (polypropylene) set up unit

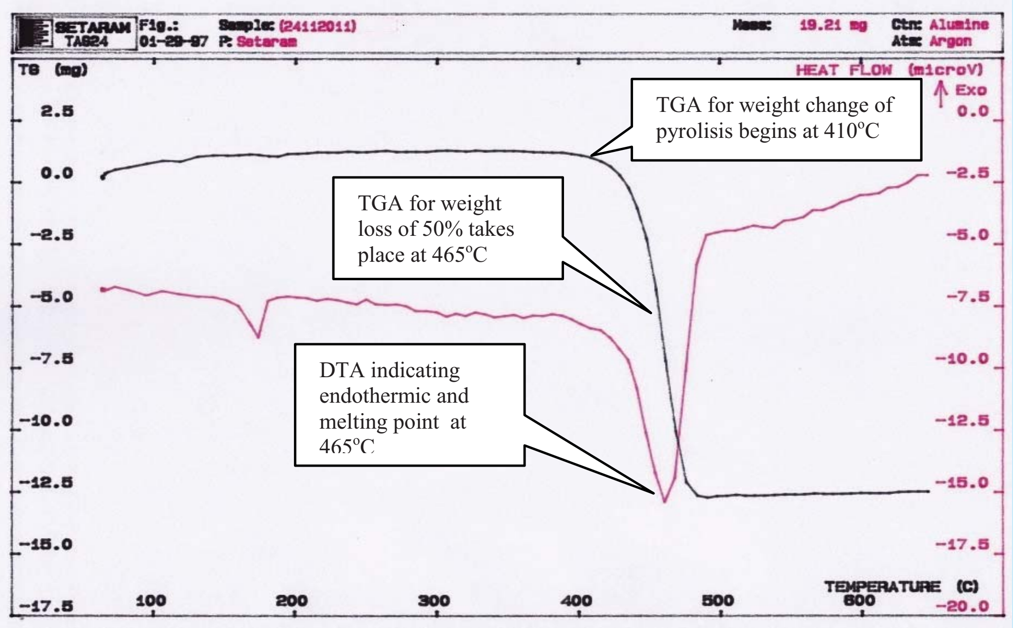

Figure 2
Thermogram of DTA-TGA for Polypropylene Plastic Waste

Table 1
Characteristics of Synthesized Catalysts and Supports
(Natural Zeolite and Activated Natural Zeolite)

Catalyst	Surface Area (m^2/Gr)	Pore volume (mL/Gr)	Pore Diameter (A^o)
ZA (natural zeolite)	37,35	0,1104	59,115
ZAA (activated natural zeolite)	71,89	0,1169	32,527
Catalyst A (NiCr4-ZAA)	84,36	0,1116	26,457
Catalyst B (NiCr6-ZAA)	72,47	0,1185	59,862
Catalyst C (NiCr8-ZAA)	64,61	0,109	67,582

temperature in a linear relationship with time (the range of temperatures between 35 and 750 °C). A sample of about 10 mg was introduced into the appropriate position of the instrument and heated at a constant rate of 10 °C min^{-1} with a nitrogen purge rate of 20 mL min^{-1} at pan.

D. Experimental Setup

The pyrolysis and catalytic pyrolysis of polypropylene plastic waste was carried out in an in-house designed stainless steel evaporator (1L volume) and fixed-bed reactor (1L volume) and the degradation experiments were performed at atmospheric pressure under nitrogen gas at different reaction temperatures. The diagram of thermal and catalytic pyrolysis of plastic waste is illustrated in Figure 1. A temperature controller was used to control the temperature of the furnace. The evaporator containing 6 g of materials was heated at 450^{o}C and purged with dry nitrogen to push the volatile products into fixed bed reactor that was already loaded with 2 g of each tested catalyst. The catalyst testing was conducted in fixed bed reactor at 400^{o}C, 450^{o}C and 500oC respectively, as dependent parameter, for 30 minutes. Thermal degradation was conducted without catalyst at the temperatur of 450^{o}C. Volatile products leaving the reactor were passed through a glass-fiber filter, followed by an ice-water condenser to collect condensable liquid products. The Tedlar bags were used to collect gaseous samples. Liquid products of pyrolysis and catalytic pyrolysis were analysed by GC–Agilent 7890A equipped with the Flame Ionization Detector (FID).

Table 2
Silica and Aluminium content in Natural Zeolite (ZA) and Activated Natural Zeolite (ZAA)

Element	Natural Zeolite, ZA (% wt)	Activated Natural Zeolite, ZAA (% wt)
Si	3.338	1.2711
Al	1.658	0.0468
Si/Al	1.954	26.243

III. RESULTS AND DISCUSSION

A. Thermal Gravimetric Analysis (TGA)

The thermal degradation of polypropylene plastic waste sample was carried out using TGA (Thermal Gravimetric Analysis) and DTA (Differential Thermal Analysis) in order to obtain the thermal properties. The TGA curve shows the variation of weight with respect to temperature was presented in Figure 2. The figure shows that the weight change due to the pyrolysis process (thermal degradation) of polypropylene plastic waste starts at the temperature of approximately 410°C and finished at 490°C. Furthermore, the weight loss of 50% (T50) occurs at 465°C as shown in TGA results. The negative value of DTA result indicates that the thermal reaction of polypropylene is endothermic.

B. Characteristic of Catalyst

Synthesized catalysts (catalyst A, B and C), activated natural zeolite (ZAA) and natural zeolite (ZA) were characterized using a variety of techniques, including nitrogen physisorption (BET), porosity, X-ray diffraction (XRD), and acidity. The surface area, pore volume, and average pore diameter values of these catalysts is listed in Table 1. Synthesized catalysts and activated natural zeolite have a high surface area when compared with natural zeolite. The HCl activation followed by calcinations treatment towards the ZA sample extremely increases its surface area. This result indicates that the activation and treatment reduce the impurities that blockage the pore mouth of the zeolite. Impregnation of metal onto the ZAA framework increases its surface area for catalyst A. However, the process of impregnation reduces the surface areas of catalyst B and C. This phenomena is possibly due to the non homogeneous distribution of metal in the ZAA surface. Some of the metal atoms may block the pore mouth of the zeolite, particularly for catalyst C which has higher metal content.

The silica (Si) and aluminium (Al) content of natural zeolite and activated natural zeolite are shown in Table 2. The Al content decreased in activated natural zeolite due to the dealumination process.

Difractograms of the zeolite (ZA and ZAA) and synthesized catalysts is shown in Figure 3. It was found that the natural zeolite consisted mainly of the mordenite type crystalline. Treatment of HCl towards the natural zeolite as well as impregnation of the Ni and Cr metal onto the zeolite did not alter the zeolite crystallinity as indicated in Figure 4. The position of the impregnated metals on activated natural zeolite is also shown in Figure 4, whereas the Ni and Cr metal are exist in bulk catalysts.

Total acid amount of the zeolite (ZA and ZAA) and synthesized catalyst samples determined by ammonia base vapour adsorption is shown in Table 3. It is exhibited that the total acid amount of the zeolite samples (ZAA) increased by the HCl treatment or after activated of natural zeolite. The similar result was reported by Trisunaryanti et.al[29] that ammonia with smaller molecular size can be adsorbed on outer and inside the zeolite surfaces. Impregnation of metals onto the ZAA sample also affected the increasing of the acidity. These results indicated that the loading of a small

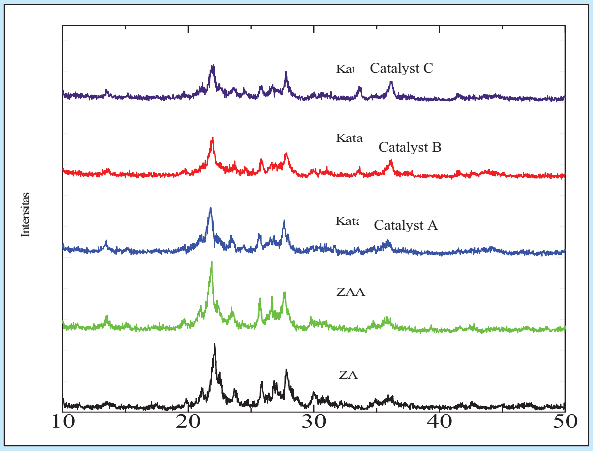

Figure 3
Difractogram of natural zeolite (ZA), activated natural zeolite (ZAA), synthesized catalyst (catalyst A, B, and C)

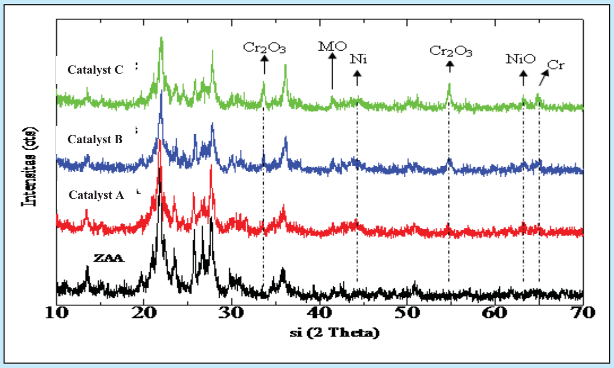

Figure 4
Difractogram of activated natural zeolite (ZAA), synthesized catalyst (catalyst A, B, and C) with the position of the impregnated metals

Table 3
Total Acid amount of Natural Zeolite, Activated Natural Zeolite and Synthesized Catalysts

Sample	Total Acid
	mmol NH_3/Gr Sample
ZA	0,7957
ZAA	1,2143
Catalyst A	1,7840
Catalyst B	1,9592
Catalyst C	1,7050

amount of metal (Ni and Cr) onto the ZAA sample performed a new acid site (Lewis acid).

C. Liquid Product Yield

In comparison with the catalytic pyrolysis, thermal pyrolysis was conducted only at the temperature of 450^{o}C which was converted directly to gasoline fraction product. Whereas, the catalytic pyrolysis of plastic waste was also carried out at varied temperature (400, 450, and 500^{o}C). Pyrolysis (non-catalytic) and catalytic pyrolysis products consists of hydrocarbon gases, liquids, and solid residue. However, gaseous products were neglected in this experiment due to problems on the gaseous capturing. Moreover the aim of this study is mainly concern on the gasoline fraction products. The solid produts as carbon residue that remained in evaporator were not also quantified. Some coke formation was observed in some experiments on catalysts surface only.

All the results of liquid fractions were analysed by GC method and compared to the commercial gasoline fractions obtained from gas stations.

The GC chromatograms of liquid fractions for thermal and catalytic pyrolysis at 450^{o}C as well as the

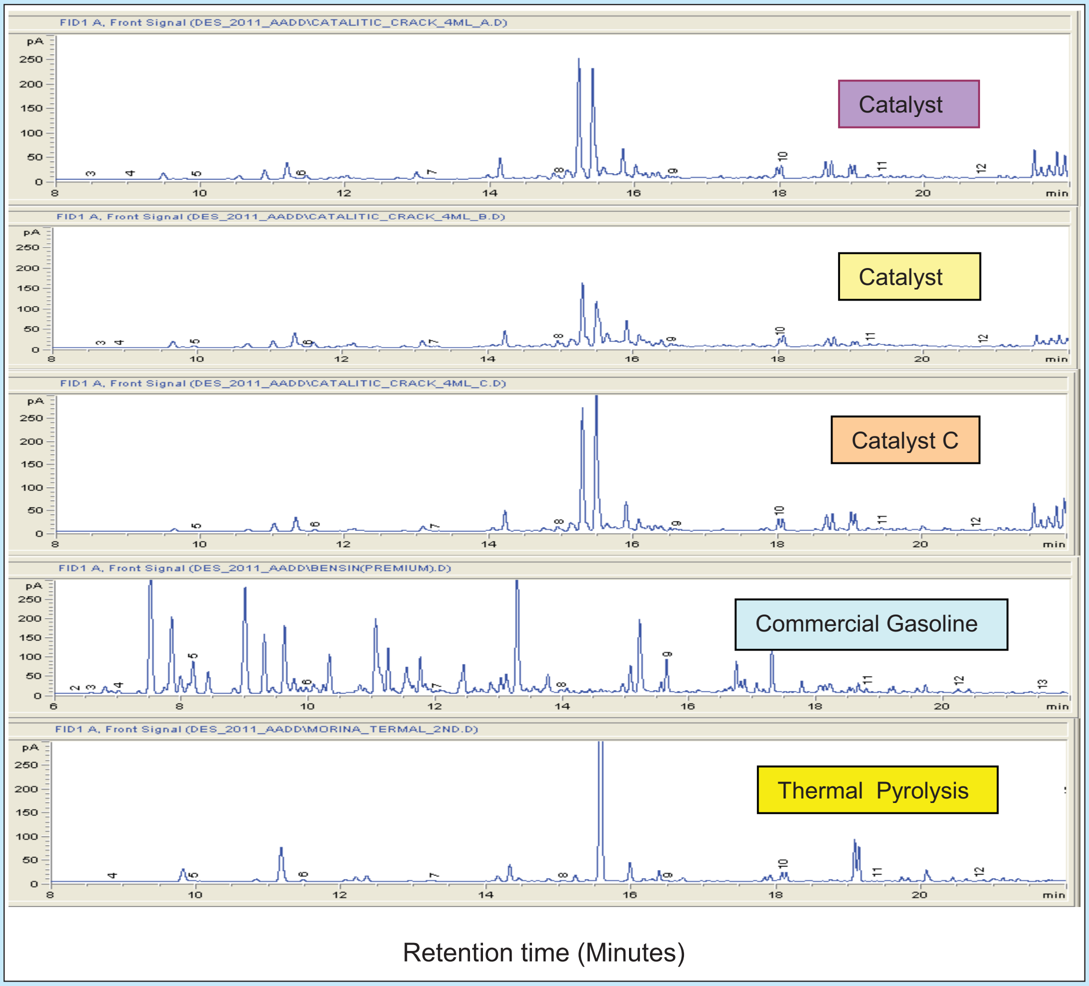

Figure 5
GC chromatogram of liquid fractions for thermal and catalytic pyrolysis at 450^{o}C that compared with commercial gasoline

Table 4A
The Carbon Number Distribution of the Liquid fraction for Conversion of Pyrolysis and Catalytic Pyrolysis of PP Plastic waste at 450°C compared with Commercial Gasoline

Number of Carbon Chain (C)	Hydrocarbon Contains, %-wt				
	Conversion at 450°C				Gasoline Fuel Commercial (Premium)
	Thermal/Pyrolysis	**Cat. A**	**Cat. B**	**Cat. C**	
3	-	-	-	-	0.11
4	0.06	0.01	0.01	0	1.04
5	1.96	1.35	3.05	0.72	21.44
6	5.02	5.53	8.92	5.02	20.85
7	2.36	6.15	10.2	3.47	18.29
8	2.98	4.48	6.25	3.97	15.83
9	27.41	37.83	38.02	40.78	10.23
10	1.84	2.42	3.17	2.07	5.51
11	4.46	6.19	6.36	6.97	2.85
12	2.35	1.47	1.86	1.64	2.48
13					1.07
14					0.3
Total	**48.44**	**65.43**	**77,84**	**64,64**	**100** **(C_5-C_{12} = 97.48%)**

Table 4B
Gasoline Fractions of Thermal and Catalytic Pyrolysis of Plastic Waste at 450°C compared with Commercial Gasoline

Components of Products	**Commercial Gasoline (Premium),%-Wt**	**Thermal Pyrolisis (Without Catalyst)**	**Catalyst A**	**Catalyst B**	**Catalyst C**
		450°C (%-wt)	**450°C (%-wt)**	**450°C (%-wt)**	**450°C (%-wt)**
(1) n-paraffin	7,62	1,32	1,32	3,22	2,04
(2) i-paraffin, naphthene, aromatic, olefin	89,86	47,12	64,11	74,62	62,6
(3) Total	**97,48**	**48,44**	**65,43**	**77,84**	**64,64**

commercial gasoline are shown in Figure 5. Table 4A and 4B show the fractions of the liquid hydrocarbon mixtures obtained from the pyrolysis and catalytic pyrolysis of the polypropylene plastic waste at 450°C in the absence of oxygen (nitrogen atmosphere).

The carbon number distributions of the liquid products based on pyrolysis (thermal degradation) and catalytic pyrolysis of PP plastic waste at 450°C are presented in Table 4A. Generally, the hydrocarbon composition of gasoline is dominated by C_5–C_{12}.

The liquid fractions produced by pyrolysis process at 450°C is approximately 48.44 %-wt. This result is lower than that produced via catalytic pyrolysis. The catalytic pyrolysis process using catalyst A, catalyst B and catalyst C produce 65.43%-wt, 77.84%-wt and 64.64%-wt respectively. Obviously, catalytic pyrolysis can improve the product selectivity and conversion of liquid fraction. It is clear that liquid

Table 5A
The Carbon Number Distribution of the Liquid fraction for Conversion of Catalytic Pyrolysis of PP Plastic waste at varied temperature reaction compared with Commercial Gasoline

Number of Carbon Chain (C)	Hydrocarbon Contains, %-wt									
	400°C			**450°C**			**500°C**			Gasoline Fuel Commercial (Premium)
	Cat. A	Cat. B	Cat. C	Cat. A	Cat. B	Cat. C	Cat. A	Cat. B	Cat. C	-
3	-	-	-	-	-	-	-	-	-	0.11
4	1.83	0.22	0.53	0.01	0.01	0	0.01	0.01	0.01	1.04
5	1.92	0.12	0.34	1.35	3.05	0.72	1.26	2.42	1.65	21.44
6	10.65	3.02	5.24	5.53	8.92	5.02	4.56	7.01	6.52	20.85
7	8.21	2.83	4.12	6.15	10.2	3.47	6.47	8.28	6.34	18.29
8	15.32	4.35	16.43	4.48	6.25	3.97	6.52	5.03	8.53	15.83
9	21.07	37.22	24.79	37.83	38.02	40.78	39.94	38.07	40.56	10.23
10	2.01	2.67	2.53	2.42	3.17	2.07	4.48	3.02	2.98	5.51
11	5.24	7.13	6.49	6.19	6.36	6.97	7.67	4.24	6.99	2.85
12	1.48	1.39	1.61	1.47	1.86	1.64	1.45	1.91	1.87	2.48
13	-	-	-	-	-	-	-	-	-	1.07
14	-	-	-	-	-	-	-	-	-	0.3
Total	**67.73**	**58,95**	**62,08**	**65.43**	**77,84**	**64,64**	**72.36**	**69.99**	**75.45**	**100** **(C_5-C_{12} = 97.48%)**

Table 5B
Conversion of Catalytic Pyrolysis of Plastic waste (PP) into Gasoline fraction at varied temperature reaction compared with Commercial Gasoline

Components of Products	**Commercial Gasoline (Premium), %-wt**	**Catalyst A**			**Catalyst B**			**Catalyst C**		
		400°C (%-wt)	**450°C (%-wt)**	**500°C (%-wt)**	**400°C (%-wt)**	**450°C (%-wt)**	**500°C (%-wt)**	**400°C (%-wt)**	**450°C (%-wt)**	**500°C (%-wt)**
(1) n-paraffin	7,62	9,83	1,32	9,13	0,64	3,22	10,89	13,04	2,04	8,46
(2) i-paraffin, naphthene, aromatic, olefin	89,86	57,90	64,11	63,23	58,31	74,62	59,1	49,04	62,6	66,99
(3) Total	97,48	**67,73**	65,43	72,36	58,95	**77,84**	69,99	62,08	64,64	**75,45**

fraction for thermal pyrolysis was quite low at 450°C since the pyrolysis required temperatures of 500-700°C. It was also observed that the catalyst B (NiCr6-ZAA), lead to increase the amount of the liquid fraction. The relative total amounts of liquid fraction (gasoline fraction) are approximately equal for catalyst A and C, and they are only different in component fractions, whereas catalyst A produces n-paraffin less than catalyst C. However, catalyst A produces the mixture of i-paraffin, naphthene, aromatic, and olefin little bit more than catalyst C. The acidity of the catalyst plays important role in the pyrolysis reaction as indicated by the results of the gasoline fraction of catalyst B in comparison with catalyst A, catalyst C and thermal pyrolysis. The acidity of catalyst B is higher than the acidity of either catalyst A or catalyst C as shown in Table 3.

The n-paraffin resulted in these experiments is still low, because the acidity of the catalyst used causes cracking reaction for hydrocarbons particularly linear or normal-paraffin, therefore, it is expected that more cracking reaction will occur on n-paraffin composition in plastic waste.

The addition of nickel (Ni) and chromium (Cr) increases the catalyst acidity significantly. As a result, the conversion is improved. Chromium (III) oxide can act as Lewis acid. The role of nickel is to harmonize the acidity and expected that dehydrogenation and dehydrocyclisation reactions occur significantly. Several studies have reported that in order to improve the catalytic performance of catalyst materials, addition of other component such as aluminum and other metal ions (Fe+3, Pd+4, V+5, etc.) into the framework of the catalyst is needed. The addition of those components takes into account to create Brönsted or Lewis acid sites to solve the problem of the low acidity of catalyst.

The results of GC analysis on liquid fractions of catalytic pyrolysis of the plastic waste at varied

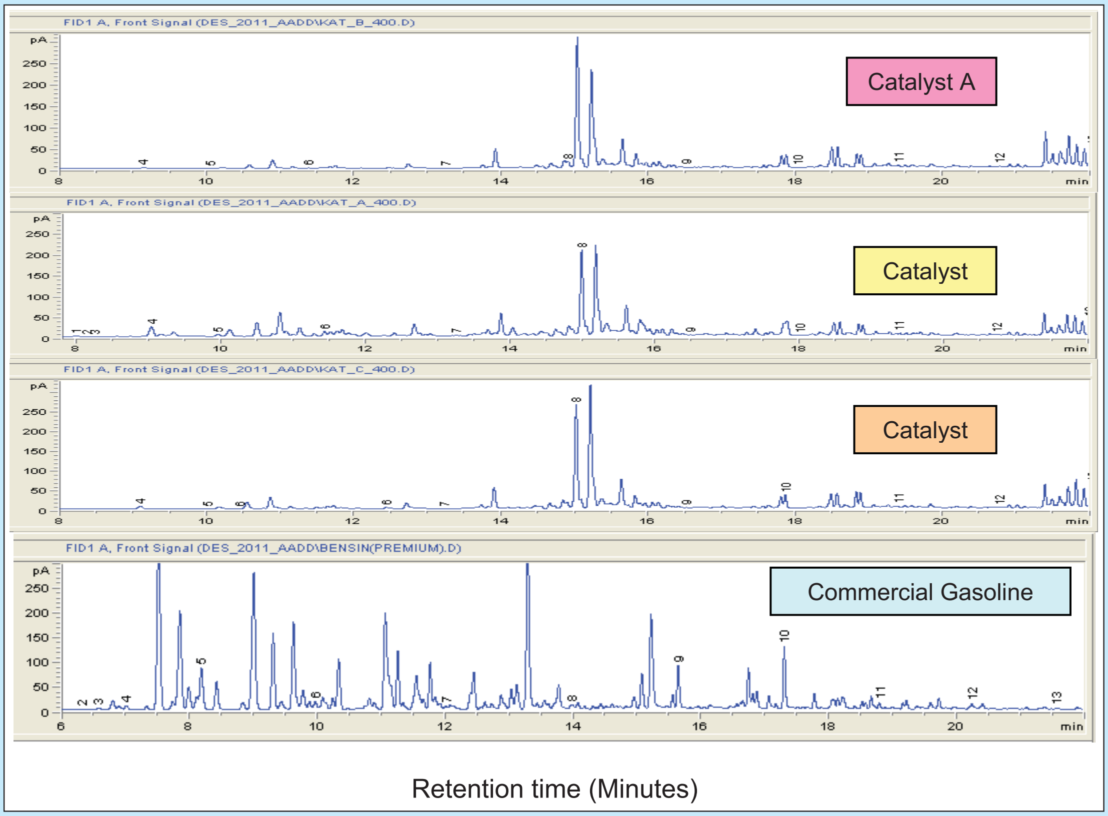

Figure 6
GC chromatogram of liquid fractions for catalytic pyrolysis at 400°C that compared with commercial gasoline

temperature reaction (i.e. 400, 450, and 500^{o}C), and the commercial gasoline, are shown in Table 5 (Table 5A and 5B). GC chromatogram of liquid fractions for catalytic pyrolysis at 400^{o}C and commercial gasoline is shown in Figure 6. The carbon number distributions of liquid products for catalytic pyrolysis of PP plastic waste at varied temperature (i.e. 400, 450, and 500^{o}C) are presented in Table 5A. According to this tables, catalyst A produces total liquid (gasoline) fractions higher at the reaction temperature of 400^{o}C than catalyst B and C. Meanwhile, catalyst B produces total liquid (gasoline) fractions higher at the reaction temperature of 450^{o}C than that produced by catalyst A and C. However, catalyst C produces total liquid (gasoline) fractions higher than that produced by catalyst A and B at the reaction temperature of 500^{o}C. At 500^{o}C, the activity of catalyst C increases due to the higher chromium (Cr) content than that contain in catalyst A and B. Furthermore, it also affect the degradation of plastic waste at the temperature of 500^{o}C. The components of liquid fractions that are produced by synthesized catalysts and thermal pyrolysis are similar with the components of commercial gasoline. Based on the results of this study, catalyst B containing 6% of chromium and 4% of nickel is the best catalyst applicable for catalytic degradation of plastic wastes to liquid (gasoline) fractions.

IV. CONCLUSION

The consumption of plastics has been continuously increasing and will be increasing in the future due to great differences in their consumption between developed and developing countries. Therefore, the amount of these types of wastes as the municipal solid wastes, will also be increasing. Growing awareness of people on environment and law will make it impossible to dispose of such wastes on landfills.

On the basis of resulted liquid fraction as gasoline fraction produced by both pyrolysis and catalytic pyrolysis of propylene plastic waste indicates that plastic wastes of the municipal solid wastes are good promising resources for production of liquid fuels. In addition, the catalytic pyrolysis process developed in this study might be used as an alternative method for solving the environmental problems due to the municipal plastic wastes, rather than dispose on landfill or incinerate in an incinerator. Plastic wastes, therefore, seems to be good resources for energy production particularly for gasoline fraction.

Natural zeolite resources are abundant in Indonesia and valuable for support or as catalyst for pyrolysis (degradation) of plastic waste. The acidity of natural zeolite can be improve by addition of nickel and chromium metals as well as a catalyst for conversion of propylene plastic waste to valuable products.

Catalyst with 6% of chromium content and 4% of nickel content and activated natural zeolite as a support to be a good catalyst in process of polypropylene plastic waste to gasoline fraction. Catalytic conversion using the catalysts based on natural zeolite, incorporation of chromium (Cr), may be use as an alternative method for recycling plastic wastes to more valuable and fuel oil.

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