

Catalytic and Non-Catalytic Depolymerization of Mixed Plastic Waste to Fuel Using Spent RFCC Catalyst

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Abstract. Environmental problems and world energy crisis have been hot issues recently that can frighten our life in the future. Plastic waste has long been seen as one that contributes to the environmental problem due to non-biodegradable properties. The amount of the waste increases significantly from year to year. It seems we can not stop the trend due to the benefit obtained from the plastic uses, i.e. cheaper, easier, and flexible. On the other hand, energy sources, such as crude oil, decreases dramatically and can not be renewed. The research on catalytic and non-catalytic depolymerization of mixed plastic waste was conducted as a part of efforts in finding a solution to the problems by converting the waste to fuel oil and gas. Spent RFCC catalyst from Pertamina refinery unit was used as a cracking catalyst for the polymer chains. The mixed plastic waste consisted of PE, PVC, PS and PP with following composition subsequently 41%, 4%, 19% and 19%. The depolymerisation products were characterized using GC-MS machine. Their Physical properties were determined by measuring the flash point, cloud point, calorific value and density. The results showed that fuel oil from the catalytic depolymerization of the plastic waste was identified as gasoline from the point of view of hydrocarbon composition. While the oil product from the non-catalytic pyrolysis showed a wider range of hydrocarbon composition. The gas composition from both catalytic and non catalytic process was comparable to Syngas.

Keywords: Plastic waste; fuel oil; depolymerization; RFCC

Introduction

Generally, Plastic waste can be reused or recycled to form various new products due to easily remelted and reformed. Such properties of municipal plastic waste which is mostly come from household, market, street, and industrial waste should not make a serious problem. However, the bad habits of throwing away plastic waste, a weak management of plastic waste and a weak law enforcement result in a major problem for the environment. One solution to resolve the problem is to recover plastic chemicals by catalytic degradation of the polymer. Plastic is derived from petroleum and can be restored to its

original form by degradation of the polymer with the help of heat and catalyst.

Zadgaonkar has developed a cracking process for mixed plastic waste using a catalyst made from a mixture of zeolite component faujasite (5-35 wt%), pseudoboehmite alumina (10-40 wt%), polyammonium silicate (1-10 wt%), and kaolin(15-60 wt%) [1,2]. While Lee Kyong-Hwan has studied the pyrolysis of plastic waste using a spent catalyst of Fluid Catalytic Cracking (FCC), which commonly used for light crude oil cracking. The pyrolysis product obtained is in the range of C₇-C₃₀ with liquid conversion of about 70-80% [3-5].

Our research here studied the pyrolysis of plastic waste using a spent catalyst of Residual Fluid Catalytic Cracking (RFCC) from the cracking process of Pertamina refinery unit, Indonesia. FCC and RFCC catalysts differentiated by their feeds. Pertamina RFCC unit specifically cultivate heavy fractions of crude oil residue with a low economic value to products with a high economic value.

The use of spent RFCC catalyst is an effort to reduce the incurred cost compared to uses of new catalyst. Direct contact between plastic melt and catalyst occurs continuously during the depolymerisation process and lead to rapid deactivation of the catalyst, hence the depolymerisation takes more catalyst and results in high operational costs.

Meanwhile, 10-15 tons per day RFCC catalyst disposed as waste at Pertamina refinery and left mounting without any treatment or solutions. It occupies a large area for the waste storage and is a burden for Pertamina. The use of the spent RFCC catalyst for large scale of plastic waste depolymerization could be beneficial for Pertamina and the environment.

Experimental

Raw material and catalyst

PE, PVC, PS, and PP wastes were used as raw materials. PE was taken from shampoo packaging waste and electronic device plastic wrap, polyvinyl chloride (PVC) from the pipe, polystyrene (PS) from protective material for electronic and polypropylene (PP) from waste packaging and plastic cups of instant noodles. The composition of mixed plastic waste [6] were 41% PE, 4% PVC, 19% PS and 36% PP. The spent RFCC catalyst was obtained from Pertamina Refinery in Balongan, West Java, Indonesia, and regenerated with air stream and stirred for 4 h with heating temperature up to 400°C.

Reaction

Pyrolysis process was carried out in two stages. The first stage was done at 300°C to

eliminate chlorine gas of PVC for 15 min. Followed by second stage i.e. raising the temperature to 400°C for 5 h at atmospheric pressure with heating rate 7°C/min. The mixed plastic waste used was 200 g and the catalyst 10 g. Plastics and the catalyst that had been mixed in the reactor were purged with nitrogen gas (N₂) at 20 cc/min. Liquid product as a function of lapsed times were measured by weight, and gas formed was calculated based on the balance of liquid and solid products.

Analyses

Products are classified into three phases; gas, liquid and solid. Liquid product was analyzed qualitatively using gas chromatography with mass spectrometer detector (GCMS, Simadzu QP2010 ULTRA). Column used was RTX5-MS length of 30 m and diameter 0.25 mm. Carrier gas was helium and the solvent was n-hexane (pa) with ratio 1:20. Temperature program was set as follows: initial temperature 40°C for 10 min with heating rate 8°C/min to 300°C and held for 10 min. For gas products, analyses were performed using both gas chromatography flame ionization detector (FID) and mass detector (MS). Solid residues and coal were characterized by proximate test; ash, moisture, volatile matter, and fixed carbon testing. While the ultimate test was done to determine the basic components of the solid residues and coal such as carbon content and hydrogen. Oil produced from the depolymerization process were then tested for their physical properties in various laboratories.

Results and Discussion

Spent RFCC regeneration

Regenerated RFCC were tested using BET method to determine changes in surface area and total pore volume. Table 1 shows the result before and after the catalyst regenerated.

Table 1. Catalyst before and after regeneration.

No.	Parameter	Surface area (m ² /g)	Total pore volume (m ³ /g)	Average pore diameter (Å)
1.	Spent RFCC before regeneration	91	0.14	59.4
2.	Spent RFCC after regeneration	121	0.18	60.2

Product yield

From the graph below it can be seen that the oil recovery in the form of liquid product is

high enough, about more than 80% of the plastic waste.

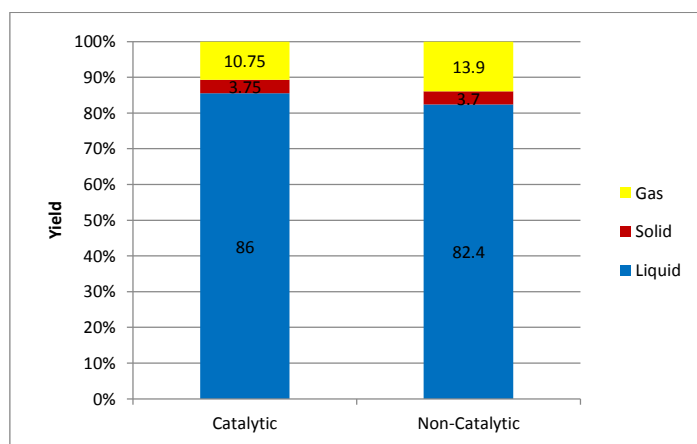


Figure 1. Yield of the mixed plastic waste.

The amount of oil produced from the pyrolysis process was strongly influenced by temperature, catalyst, reaction time, structure of polymers and polymer interactions with other polymers.

Accumulative amount of liquid product

The difference between catalytic and noncatalytic results can be seen from the accumulative liquid products produced in the graph below.

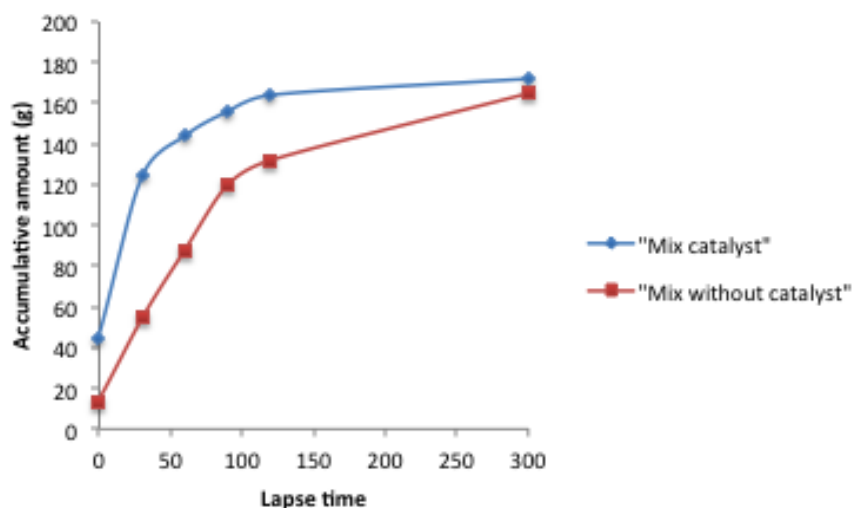


Figure 2. Accumulative liquid products from the pyrolysis of mixed plastic waste.

At interval 30-60 min, oil production from catalytic process is twice as those from the non-catalytic process. This shows that the catalyst in the depolymerization process of plastic waste can accelerate the reaction rate and liquid production. Additionally, RFCC

catalyst also serves to break the polymer chain into lighter hydrocarbons as seen in Fig. 3.

Total carbon distribution

Generally gasoline has a carbon number range from C₆ to C₁₂ while kerosene from C₁₂ - C₂₀ and diesel from C₂₁ to C₃₀[7]. The amount of carbon also affects physical properties of oils such as molecular weight, boiling point, density and others.

Fig. 3 shows the carbon number distribution of oil in the catalytic and non catalytic depolymerization of mix plastic waste. Total carbon by catalytic pyrolysis mix plastic had a fairly narrow range, that was C₇ to C₁₅, and hydrocarbons above C₁₆ were not detected. 86.2% of the oil product was light oil fraction of C₇ - C₁₁, the rest was the fraction of C₁₂ - C₁₅. Unlike the catalytic, the noncatalytic depolymerization produced an oil that had carbon number spread evenly from C₇ to C₂₁, in which 30.8% of it was in the form of heavy oil with carbon number more than 16.

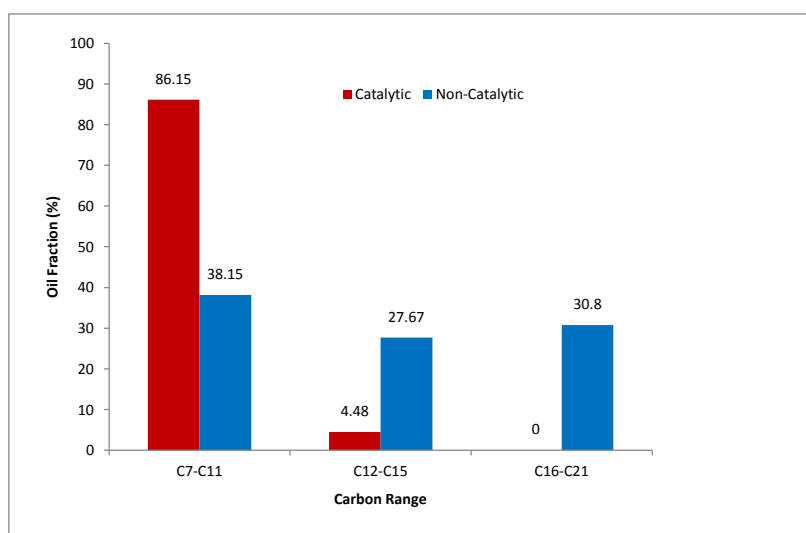


Figure 3. Hydrocarbon distribution of liquid product.

PONA distribution

PONA distribution means the composition of Paraffin, Olefin, Naphtene and Aromatic in the oil product. For catalytic process, aromatic compounds produced was 80.8% while the olefin and paraffin, respectively 16.5 and 2.5%.RFCC catalyst consisting of microporous zeolites and mesoporous silica-alumina. It can break the chain of the polymer easily into lighter hydrocarbon components. Micro and mesopores in the catalyst control the distribution of the product formed by the gradual diffusion of olefin intermediates resulting in cyclization to form aromatic compounds [3].

On the other hand, for noncatalytic process the type of hydrocarbon produced was more

evenly distributed, and naphthene was not formed at all. Olefin compound was 47.2%, paraffin and aromatic compounds, respectively 39.2 and 13.6%. Effect of catalyst absence can be seen from the olefin intermediate that was difficult to form aromatic instead stabilized to form paraffin and olefin.

Gas product composition

Analysis of gas formed during catalytic depolymerization process of mixed plastics can be seen in table 2 and 3. GC-FID was used to identify gases of low molecular weight and GC-MS was used to identify gases of high molecular weight.

Table 2. Gas content with GC-FID.

No.	Gas	Molecular formula	Content (%)	Flash point (°C)
1.	carbondioxide	CO ₂	5.87	-
2.	carbonmonoxide	CO	3.38	-191
3.	Nitrogen	N ₂	76.83	-
4.	Oxygen	O ₂	-	-
5.	Hydrogen	H ₂	7.03	-253
6.	Methane	CH ₄	6.87	-188

Table 3. Gas content with GC-MS.

No.	Gas	Molecular formula	Content (%)	Flash point (°C)
1.	Nickel Tetracarbonyl	Ni(CO) ₄	73.80	<-20
2.	cyclopropane Carboxaldehyde	C ₄ H ₆ O	8.20	7
3.	2-Methyl Propane	C ₄ H ₈	9.14	-116
4.	2-Methyl Butane	C ₅ H ₁₂	1.24	-51
5.	Pentane	C ₅ H ₁₂	3.71	-50
6.	1,2-dimethyl Cyclopropane	C ₅ H ₁₀	1.45	-53.9
7.	2-Methyl Pentane	C ₆ H ₁₄	1.06	-53.9
8.	2-Methyl-1- Pentene	C ₆ H ₁₂	0.96	-23.33
9.	4-Methyl-2- Pentene	C ₆ H ₁₂	0.43	-27

Solid Characterization

Solid residue can be used as raw material to produce solid fuels. Table 4 shows the characteristics of the solids formed from the pyrolysis process.

Table 4. Analysis of residue.

Parameter	Value	Unit
Humidity	5.83	%
Ash	41.84	%
Volatile matter	28.34	%
Fix carbon	23.99	%
Total Carbon	45.63	%
Total Hydrogen	4.33	%
Calorific value	4460	Kcal/Kg

Comparison with commercial products

Physical properties tested were flash point, cloud point, calorific value, density, and boiling point. Table 5 shows a comparison of the physical properties of the oil from pyrolysis

Table 5. Physical properties compare to commercial.

Parameter	Catalytic	Non-catalytic	Gasoline*	Kerosene*
Flash point (°C)	28	28	23	53-80
Cloud point (°C)	< -20	< -20	< -20	< -15
Calorific value (MJ/kg)	44.35	-	42-46	42-45
Density (g/mL)	0.8	0.8	0.71-0.77	0.82-0.85
BP (°C)	83-163	110-345	30-300	147-300

Conclusion

The results showed that fuel oil from the catalytic depolymerization of the plastic waste had narrow carbon range and was identified as gasoline from the point of view and hydrocarbon composition. Catalytic process also gave higher production rate of liquid product comparing to non-catalytic one. While the oil product from the non-catalytic pyrolysis showed a wider range of hydrocarbon composition. The gas composition from both catalytic and non catalytic process was comparable to syngas.

- [1] Zadgaonkar, A. *A Catalyst Composition For Catalytic Cracking of Waste Plastic*. International Application Published Under The Patent Cooperation Treaty (PCT). World Intellectual Property Organization. **2005**
- [2] Zadgaonkar, A., Umesh. *ENVIS*. **2004**, 2(5).
- [3] K.H. Lee., N.S. Noha, D.H. Shina., Y. Seob. *Polym. Degrad. Stab.* **2002**, 78, 539.
- [4] Lee, K. H., Sang-Gu, J., Kwang-Ho, K., Nam-Sun, N., Dae-Hyun, S., Jaehyeon, P., Younghwa, S., Jurng-Jae, Y., and Geug-Tae, K. *J. Chem. Eng. Korea Institute of Energy Research*. **2003**, 20(4), 693.
- [5] Lee, K. H., Dae-Hyun, S. *Korean. J. Chem. Eng. Korea Institute of Energy Research*. **2006**, 23(2), 209.
- [6] A. López, I. de Marco, B.M. Caballero, A. Adrados, M.F. Laresgoiti. *Waste. Manage.* **2001**, 31, 1852.
- [7] Ali, E, “*Improvement of Gasoline Octane Number by Blending Gasoline with Selective Components*”. Thesis. University of Technology-Baghdad. **2008**.