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# HYDROCARBON FRACTIONS OBTAINED FROM RECYCLING OF WASTE MATERIALS

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Pyrolysis of contaminated waste plastics was carried out in a laboratory scale batch reactor at 450 °C under nitrogen atmosphere. Raw materials were original high density polyethylene (HDPE) and waste motor oil flasks from industrial sector. Volatile products were passed through a fixed catalyst bed with temperature of 350 °C. In the experiments Y-zeolite, β-zeolite, HZSM-5, Co/Mo and Ni/Mo catalysts were used. Three product fractions were obtained: gas, liquid and heavy oil. Catalysts had mainly effect on the gas and liquid yields, the amount of the residue did not show significant differences in the case of the same raw material. By pyrolysis of contaminated raw material higher volatile product yield could be observed compared to pyrolysis of the original raw material. Catalysts increased gas yields and had influence on the composition of products. Most significant effect could be observed in the case of Y-zeolite and β-zeolite catalysts. Contaminant level of liquid products could be decreased in case of thermo-catalytic pyrolysis, which is a key property for further application of the pyrolysis products.

**Keywords:** pyrolysis, contaminated plastic waste, heteroatom removal, catalyst

## Introduction

In the last decades both the amount of polymer materials and the wastes from them has shown a rapidly increasing tendency. Disposal of plastic wastes is very important because the degradation of these materials takes a very long time. Moreover plastics have very high hidden energy content. There are many possibilities for recycling plastic wastes, one of them is pyrolysis. During pyrolysis the long polymer chains of plastics are degrading into smaller hydrocarbon molecules in absence of oxygen and in the temperature range of 400–900 °C. Pyrolysis products are similar to the hydrocarbon-fractions generated in an oil refinery, therefore they can be used as fuels or petrochemical feedstock [1-4]. By pyrolysis of plastic wastes the saving of crude and energy and reduction of $CO_2$ emission is possible.

Plastic wastes usually have heteroatom as contamination (e.g. sulphur, nitrogen or chlorine containing substances) on their surface or in their own material. Chemical recycling of contaminated plastic wastes is possible, but contaminants present problem because they appear in the products. Many researchers have investigated the composition of products derived from pyrolysis of different contaminated plastic materials [5-8]. In most of the studies were used raw materials, which had contamination in their own material (heteroatom containing plastics or additives) but pyrolysis of plastic wastes, which contain heteroatom containing substances on their surface was slightly studied.

In terms of further energetic utilization there are limits for heteroatom containing substances in the products. Therefore reduction the amount of the contaminants in the products is very important because by that procedure the range of raw materials could be widened (e.g. contaminated plastic wastes could be also recycled this way). The catalyst application is one possible way for decreasing the heteroatom content in the products. Catalysts are capable both to absorb heteroatom containing substances and change the composition of the products by taking over the heteroatoms in the gas phase. Many researches were carried out to examine the efficiency of different catalysts [9-13]. In many works there were used catalysts in vapour phase contact with the products. It means that only volatile products are getting to the catalyst bed therefore catalysts affect only the composition of the volatile products. The applied catalysts decreased the chlorine and nitrogen content of pyrolysis oils even by 90% or more.

In this work pyrolysis of contaminated plastic waste was carried out at 450 °C. Volatile products were driven trough different catalysts in order to decrease the concentration of heteroatom containing substances in the liquid products. The applied catalysts are widely used in the industry, too.

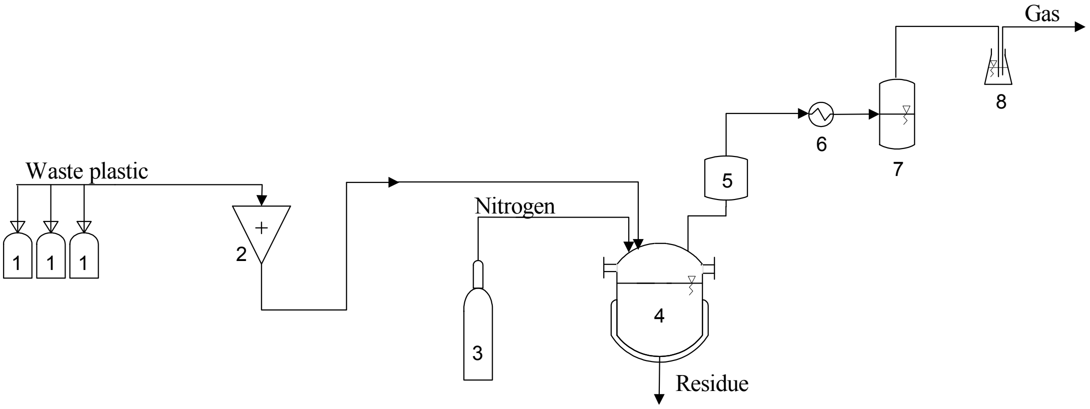

*Figure 1:* The layout of the process:
1. Raw material, 2. Shredding and grinding, 3. Nitrogen bottle, 4. Reactor,
5. Catalyst bed, 6. Cooler, 7. Liquid product receiver, 8. Water trap

## Experimental

### *Raw materials*

Motor oil flasks were obtained from Design Kft. The flasks were shredded and grinded into particles up to 3 mm diameter. Composition of the raw material was followed by Fourier-Transformed Infrared Spectroscopy. It was found that the main component of that was HDPE (88.6 wt%). In addition the raw material contained significant amount of motor oil contamination (7.2 wt%) and adsorbed water (0.6 wt%).

The rest (3.6 wt%) was foil of the motor oil flasks, which had the following composition: 53.3 wt% PP, 40.0 wt% PVC and 6.7 wt% HDPE. For comparison experiments were done also with original, off-grade HDPE, obtained from TVK Co.

### *Catalysts*

Five different catalysts were applied in order to improve the product qualities: Y-zeolite, HZSM-5, β-zeolite, Co-Mo, and Ni-Mo.

*Table 1:* Properties of the applied catalysts

| | BET surface, $m^2/g$ | Si/Al | Microporous surface, $m^2/g$ | Acidity, meq. of $NH_3/g$ |
|---|---|---|---|---|
| Y-zeolite | 205 | 45 | 127 | 0.61 |
| HZSM-5 | 322 | 31 | 198 | 0.55 |
| β-zeolite | 446 | 33 | 384 | 0.47 |
| Co-Mo cat. | 196 | 12 | 99 | 0.28 |
| Ni-Mo cat. | 177 | 14 | 74 | 0.26 |

The first two are commonly used cracking catalysts having isomerization function and the last two are bifunctional catalysts with hydrogenization/dehydrogenization function. Properties of the catalyst are shown in *Table 1.*

Before the experiments catalysts were heated at 500 °C in nitrogen atmosphere for 4 hours.

### *Pyrolysis process*

Pyrolysis was carried out in a batch reactor with 2.0 $dm^3$ volume. The layout of the process is shown in *Fig. 1.* The raw material was first shredded and grinded after that it was fed into the reactor. In every experiment 400 g of raw material was pyrolized in nitrogen atmosphere. The reactor temperature was 450 °C in every case. Above the reactor a fix catalyst bed was placed. The temperature of the catalyst bed was 350 °C. Volatile products generated during pyrolysis were passed over the catalyst bed after that they were cooled and condensed in a vessel. The non-condensable products (gases) were blown through a water trap to collect the inorganic substances. All of the experiments were taken 150 minutes, after that the reactor was cooled and residue (heavy oil) was taken off at the bottom of the reactor. The reactor and the catalyst bed were electrically heated, measurement of temperature occurred with thermocouples.

### *Analysis of pyrolysis products*

A DANI gas-chromatograph fitted with a 30 m x 0.53 mm Rtx-1 column was used for hydrocarbon analysis of pyrolytic oils.

Composition of the raw material was analyzed by a TENSOR 27 type Fourier transformed infrared spectrometer in the 4000–400 $cm^{-1}$ wave number ranges.

For chlorine determination a Mitsubishi TOX-100 type instrument was used. The temperature was 900 °C, and argon was used as inert gas.

Determination of nitrogen and sulphur content of fractions were performed by using standardized methods: ASTMD 6428 99 and ASTMD 6366 99, respectively.

## Results and discussion

### *Product yields*

During pyrolysis three different products were obtained: gas, liquid and heavy oil. Product yields are shown in *Figs 2* and *3*.

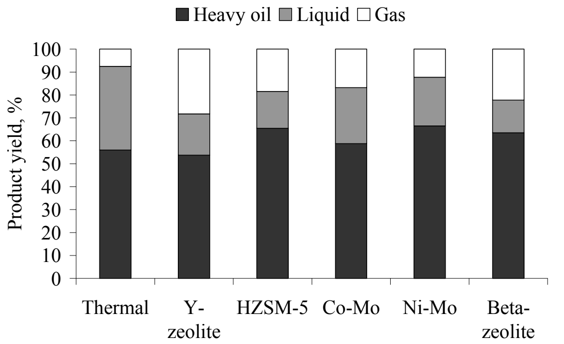

*Figure 2:* Product yields obtained during pyrolysis of the original raw material

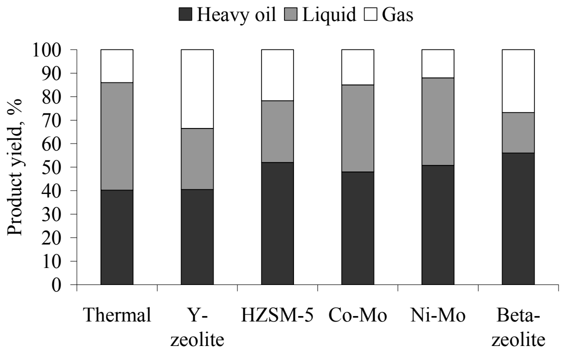

*Figure 3:* Product yields obtained during pyrolysis of the motor oil flasks

In the case of the different raw materials different product yields were observed. From the contaminated raw material more volatile products were obtained (gas yield changed between 12.0 and 33.5 wt% and yield of liquid product was between 17.2 and 45.7 wt% in the case of the motor oil flask raw material, while in the case of the original raw material those values were only 7.5–28.2 wt% and 16.0–36.5 wt%).It is important to remark that the difference between the volatile product yields from the two raw materials was more then the amount of volatile contaminations (water and oil) on the surface of the motor oil flasks. The reason of that could be explained by the theory that the contaminations have initiated the decomposition of other polymers at lower temperatures, because they were able to given free radicals at lower temperature. This way the activation energy of the pyrolysis decreased in the case of the contaminated raw material. In other words at the same temperature more volatile products could be obtained. If the yields in the thermal and thermo-catalytic cases are compared it could be seen that the volatile product yields are higher in almost every times in the thermal cases than in the thermo-catalytic cases. It is similar result with the works of others [14] but the cause of the phenomena was not explained in the mentioned reference. Probably it might be because of the changed flow conditions but to clarify that needs more investigations. Yields of the gases are higher in the thermo-catalytic cases compared to the thermal cases. It is due to the secondary cracking on the catalyst bed. The strongest effect had the Y-zeolite in the case of the same raw material because this catalyst has the largest micro-porous surface.

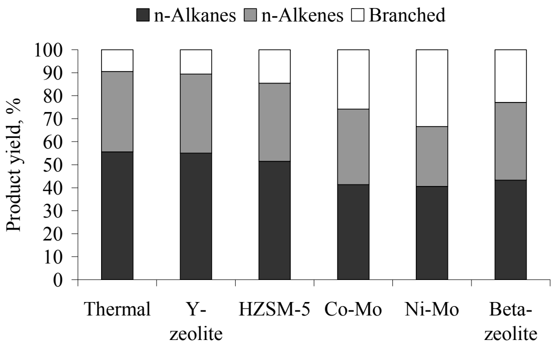

*Figure 4:* Composition of gases obtained from original raw material

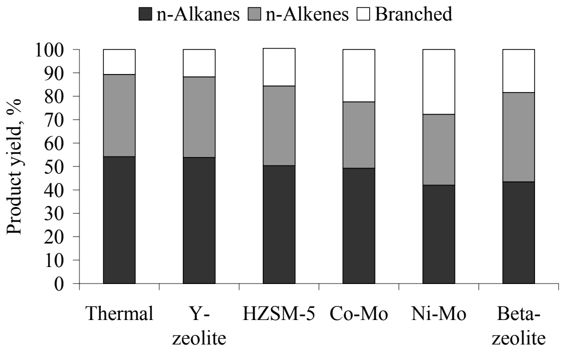

*Figure 5:* Composition of gases obtained from motor oil flasks

The molecules of the liquid fraction can fit only in the micropores where secondary cracking reactions are taking place therefore micro-porous surface has a strong effect on the yields.

### *Composition of gases*

Carbon number distribution analysis of gases showed that gas products were in the carbon number range $C_1$-$C_6$. The gas phase contained $C_6$ hydrocarbons because the not complete condensation. Most of the gases (65–80 wt%) was in the $C_3$-$C_4$ fraction. Composition of gases was analyzed by gas-chromatography and the results are shown in *Figs 4* and *5*. In all of the cases n-alkanes, n-alkenes and branched hydrocarbons were detected. In the figures it could be clearly seen that composition of gases obtained from the different raw materials do not show significant differences. Thus, the composition of the raw material has not effect on the composition of the gas product but the applied catalysts affected it. Namely the amount of branched hydrocarbons in the gas phase increased in the thermo-catalytic cases that could be explained by the isomerization effect of the used catalysts. Isomerization was the strongest in the case of the Co-Mo and Ni-Mo catalysts, the increase of the branched substances was 16.3 and 23.9% in the case of the original raw material and 11.7 and 17.0% in the case of the motor oil flasks compared to the gases obtained from the thermal pyrolysis.

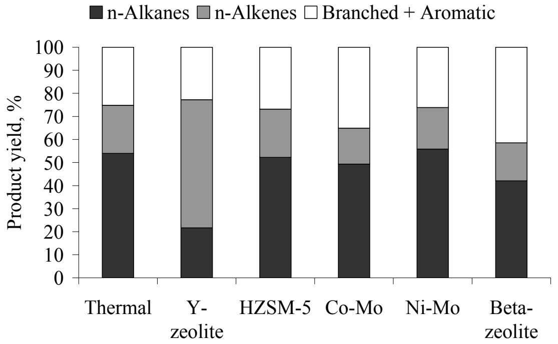

*Figure 6:* Composition of liquid products obtained from original raw material

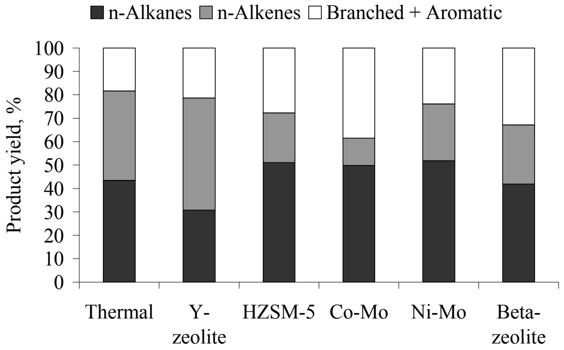

*Figure 7:* Composition of liquid products obtained from motor oil flasks

### *Composition of liquid products*

Composition and carbon number distribution of liquid products are shown in *Figs 6-7* and *Figs 8-9*, respectively. In all of the cases n-alkanes, n-alkenes, branched and aromatic hydrocarbon groups were detected. The figures clearly show that composition of the liquid products do not changes significantly with the composition of the raw material. Except of the liquid products obtained by using Y-zeolite catalyst the samples contained around 50% n-alkanes. When Y-zeolite was used, most of the liquid product was unsaturated. The amount of branched and aromatic compounds increased in the thermo-catalytic cases.

This could be explained by the isomerization effect of the catalysts. The strongest isomerization could be observed in the case of the Co-Mo and β-zeolite catalysts. They caused 9.9 and 16.3% or 20.2 and 14.6% differences in the amount of branched and aromatic hydrocarbons in the case of the original and motor oil flask raw materials compared to the thermal cases.

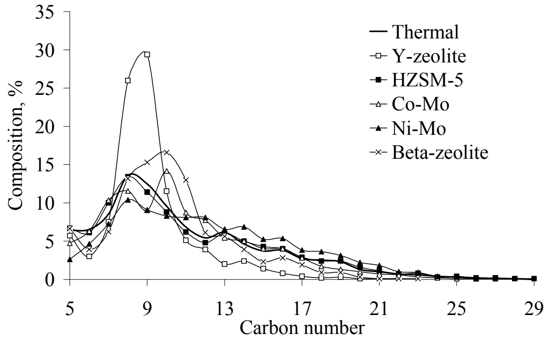

*Figure 8:* Carbon number distribution of liquid products obtained from original raw material

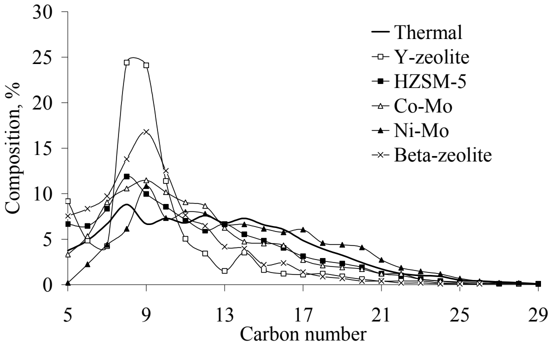

*Figure 9:* Carbon number distribution of liquid products obtained from motor oil flasks

Liquid products were in the carbon number range $C_5$-$C_{29}$. If catalysts with cracking function were applied, the average carbon number of the liquid product decreased. It means that the amount of the lighter compounds increased and the amount of the heavier hydrocarbons decreased in the oil. This was slightly more apparent in the case of original raw material than in the case of motor oil flasks because the contaminants decreased the activity of the catalysts. The reason of the decrease in the average molecular weight is the secondary cracking of the liquid product on the catalyst bed. The greatest effect had the Y-zeolite catalyst that enlarged mainly the $C_8$-$C_9$ fraction (more than 50 wt% of the samples were $C_8$-$C_9$ hydrocarbons). This could be explained by the large macro-porous surface of the Y-zeolite.

### *Contaminant level of liquid products*

Chlorine and nitrogen content of liquid product was measured. Reduction in contaminant level of the liquid products by catalysts in the case of liquids obtained from contaminated raw material is shown in *Fig. 10*.

Chlorine and nitrogen content of liquid products derived from pyrolysis of original raw material was negligible therefore it is not included in the diagram. Reduction in contaminant level was calculated from the contaminant level of the liquid products obtained from thermo-catalytic pyrolysis compared to the liquid from the thermal case. It is clear that significant reduction could be reached both in chlorine and nitrogen content using catalysts. In chlorine content there was 45–84% and in nitrogen content 20–60% decrease. The Co-Mo catalyst had the most significant effect in case of both heteroatoms. However, it is important to note that in all of the experiments there were used fresh catalysts and the decrease in the activity and the regenerability of these catalysts was not studied, it is the aim of our future work.

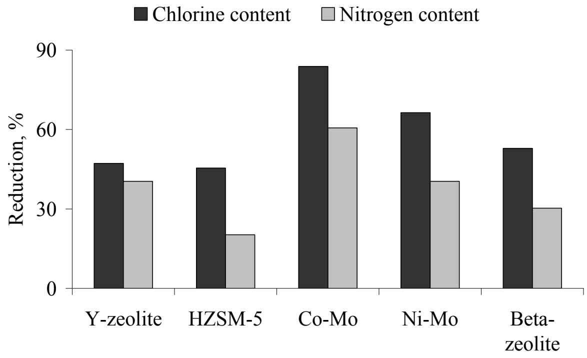

*Figure 10:* Reduction in chlorine and nitrogen content of liquid products by catalysts

## Conclusion

In this work thermal and thermo-catalytic pyrolysis of contaminated raw materials was investigated. The ability of five different catalysts for improving the quality of the liquid products and decrease the contaminant level of them was examined. Between the volatile products and the catalyst it was a vapour phase contact. The product yields did not show significant differences in thermo-catalytic cases compared to the thermal cases but the applied catalysts had favourable effect on product qualities. The amount of branched hydrocarbons in gas and liquid products increased in the thermo-catalytic cases and the catalysts with cracking function decreased the average molecular weight of the liquid products. These changes are advantageous in terms of energetic utilization. Contaminant level of liquid products could be decreased significantly by catalysts but further investigation is needed in view of changes in activity of catalysts in time.

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## REFERENCES

1. N. Miskolczi, L. Bartha, G. Deák, B. Jóver, D. Kalló: Thermal and thermo-catalytic degradation of high-density polyethylene waste, J. Anal. Appl. Pyrolysis, 72, (2004), 235–242
2. A. Angyal, N. Miskolczi, L. Bartha: Petrochemical feedstock by thermal cracking of plastic waste, J. Anal. Appl. Pyrolysis, 79, (2007), 409–414
3. A. K. Panda, R. K. Singh, D. K. Mishra: Thermolysis of waste plastics to liquid fuel A suitable method for plastic waste management and manufacture of value added products—A world prospective, Renewable and Sustainable Energy Reviews, 14, (2010), 233–248
4. S. Kumara, A. K. Panda, R. K. Singh: A review on tertiary recycling of high-density polyethylene to fuel, Resources, Conservation and Recycling, 55, (2011), 893–910
5. T. Bhaskar, W. J. Hall, N. Merry M. Mitan, A. Muto, P. T. Williams, Y. Sakata: Controlled pyrolysis of polyethylene/polypropylene/polystyrene mixed plastics with high impact polystyrene containing flame retardant: Effect of decabromo diphenylethane (DDE), Polymer Degradation and Stability, 92, (2007), 211–221
6. T. Bhaskar, M. Tanabe, A. Muto, Y. Sakata: Pyrolysis study of a PVDC and HIPS-Br containing mixed waste plastic stream: Effect of the poly(ethylene terephthalate), J. Anal. Appl. Pyrolysis, 77, (2006), 68–74
7. F. Pinto, P. Costa, I. Gulyurtlu, I. Cabrita: Pyrolysis of plastic wastes. 1. Effect of plastic waste composition on product yield, Journal of Analytical and Applied Pyrolysis, 51, (1999), 39–55
8. A. López, I. de Marco, B. M. Caballero, M. F. Laresgoiti, A. Adrados, A. Torres: Pyrolysis of municipal plastic wastes II: Influence of raw material composition under catalytic conditions, Waste Management, 31, (2011), 1973–1983
9. M. Brebu, T. Bhaskar, K. Murai, A. Muto, Y. Sakata, Md. A. Uddin: Thermal degradation of PE and PS mixed with ABS-Br and debromination of pyrolysis oil by Fe- and Ca-based catalysts, Polymer Degradation and Stability, 84, (2004), 459–467
10. Y. Sakata, T. Bhaskar, Md. A. Uddin, A. Muto, T. Matsui: Development of a catalytic dehalogenation (Cl, Br) process for municipal waste plastic-derived oil, J Mater Cycles Waste Manag, 5, (2003), 113–124
11. N. Merry M. Mitan, M. Brebu, T. Bhaskar, A. Muto, Y. Sakata: Individual and simultaneous degradation of brominated high impact polystyrene and brominated acrylonitrile-butadiene-styrene and removal of heteroelements (Br, N, and O) from degradation oil by multiphase catalytic systems, J Mater Cycles Waste Manag, 9, (2007), 56–61

12. N. Lingaiah, Md. A. Uddin, A. Muto, T. Imai, Y. Sakata: Removal of organic chlorine compounds by catalytic dehydrochlorination for the refinement of municipal waste plastic derived oil, Fuel, 80, (2001), 1901–1905
13. A. López, I. de Marco, B. M. Caballero, M. F. Laresgoiti, A. Adrados: Dechlorination of fuels in pyrolysis of PVC containing plastic wastes, Fuel Processing Technology, 92, (2011), 253–260
14. Md. A. Uddin, T. Bhaskar, J. Kaneko, A. Muto, Y. Sakata, T. Matsui: Dehydrohalogenation during pyrolysis of brominated flame retardant containing high impact polystyrene (HIPS-Br) mixed with polyvinylchloride (PVC), Fuel, 81, (2002), 1819–1825