

CHEMICAL RECYCLING OF WASTE POLYETHYLENE AND POLYPROPYLENE

N. Miskolczi¹, L. Bartha¹, Gy. Deák¹ and B. Jóver²

¹University of Veszprém, Department of Hydrocarbon and Coal Processing

²MOL Hungarian Oil and Gas PLC, R&D, Hungary

Abstract. Chemical recycling of waste polymers is one of the possible routes of their utilization. On the other hand these materials have reusable energy content. Several cracking processes are proposed for waste plastics, the long alkyl chains of the polyolefins can be degraded and transformed into lighter and valuable hydrocarbons.

In this paper results obtained in mild cracking processes with polyolefin wastes under different conditions are presented. The influence of the raw material composition on the properties of the cracked products was studied. A horizontal tube reactor was applied as cracking reactor. It was found that the cracking parameters (e.g. type of waste polymers and residence time) affected not only the yields but also the composition of products. The olefin content of the fractions and the distribution of the double bonds were determined by gas-chromatography and infrared spectroscopy. The gas and liquid products had significant content of unsaturated hydrocarbons, mainly olefins. The fuel like liquids had low sulfur and nitrogen content.

Key words: waste polyolefins, chemical recycling, residence time, gas-chromatography, unsaturated hydrocarbons

Introduction

Plastic materials play an important role in human life in the modern society e.g. the total plastic consumption was 150Mt in 2000 worldwide and only in Europe 45Mt.

According to responsible estimates it will be 66 Mt in 2010. The amount of plastic wastes made from them was 25Mt, which will reach 35Mt in 2010 [1]. However, the utilisation of enormous quantities of wastes from environmental and energetic aspects is not solved yet. The problem is global and not divided by borders among countries. On the other hand some directives exist to reduce it. One of them suggests a minimal percent of the recyclable level of all waste, which could be minimum 60% of gross wastes amount in 2005 [2]. In the member countries of the EU recycle of 20% of plastic wastes is aimed at 2005, and 30% in 2010. Nowadays the amount of recycled waste plastics is less than 10%. Recycling is one of the three ways for utilization and minimalization of the huge amount of wastes. The others are landfilling and incineration with or without energy recovery. Neither landfilling nor incineration can solve the growing problem of huge amount of wastes, e.g. directives exist to maximize the mass of the deposable wastes. In 2005 it will be 40% of the total amount of wastes arisen in 1990 [3-4]. End gases with high content of toxic and harmful compounds can be arisen in case of incineration, therefore incinerators need special filter system with high efficiency, which can only decrease their concentration, but not eliminate. The slug of incineration containing toxic ash as well, which can also cause environmental problems.

Several methods have been suggested for solving the problem of waste plastics, but some of them are still in their initial stages, or produce further environmental pollution. One of the prospective ways of the utilisation of the waste polymers is

chemical (thermal) treatment – which is named tertiary recycling in the literature – where long alkyl chains are broken into a mixture of lighter hydrocarbons. Further utilization of these hydrocarbons has also not been solved yet. One possibility of their utilization is fuel like application or blending in fuel as mixing components. Many researchers study their application as fuel. This hydrocarbon mixture having high olefin content can be saturated with hydrogen, and perhaps isomerized by the use of catalysts. These steps result in a high quality synthetic diesel fuel, with high cetane number, and theoretically these fuels are free from sulphur, nitrogen and metals. The treatment might be only thermal or catalytic. Cracking reactions are endothermic, and have need energy. The required heat and temperature can be reduced with catalysts, but the disposal and the activation loss or regeneration of the catalysts could cause some problems [5-9].

Several researchers investigate the thermal recycling of waste polymers under different catalytic and thermal circumstances [10-15]. Their experiments were carried out at laboratory sizes (1-500g) using clean and not waste polymers. On the other hand, the effect of the cracking temperature on the properties of products is well demonstrated in the literature not only for batch reactor but also in continuous cracking. It was found earlier that the changing of the process parameters could modify both yields and the structure of the products. At higher temperatures gas and coke yields are higher, and the liquid fraction has significant aromatic and cyclic hydrocarbon content. At lower temperatures products mainly consist of liquid compounds. The other important parameter for waste polymer degradation is the residence time.

In our experiments the thermal cracking behaviour of a polypropylene, a polyethylene and the effect of residence time of product properties were investigated in a horizontal tube re-

actor. Mainly the change of olefin and paraffin content and their distribution were investigated in function of cracking parameters, because these properties mainly affect the further utilization of the liquid fractions. Liquid fractions were separated into two fractions, and their application possibilities as fuel were studied.

Experimental

Raw Materials. A commercial polyethylene (PE), and a polypropylene (PP) was used as raw materials. The polyethylene waste was obtained from agricultural foil of the plastic bags, and the polypropylene from packaging waste. Their main properties are summarized in Table 1.

Table 1. The properties of waste polymers

Properties	PE	PP
Grain size, mm	4-6	4-5
Density, g/cm ³	0.932	0.853
Ash content, %	0.67	0.61
Humidity content, %	0.13	0.28
Metals, ppm		
Ca	206	222
Zn	38	261
Ti	593	103

Each polyolefin waste has Ca, Ti, Zn content from filler materials and pigments such as CaCO₃, TiO₂ and ZnO.

Cracking apparatus. For studying the cracking of greater amounts of waste polyolefins a horizontal tube reactor has been chosen for these experiments. The cracking apparatus is shown in Figure 1. The waste polymers with suitable grain size (4-7mm) were fed in by an extruder, which was directly connected to the reactor. Both the extruder and the reactor were heated with electric heater and for the control of the temperature fitted with thermometers. After the extruder the preheated polymers were driven into the reactor, where they were melted, and the long polymer chains cracked into smaller fragments. The temperature inside the tube reactor was kept at 525°C. Reaction products (liquid and gases) got into a separator of vapours and

residue. Volatile products obtained from the separator were partially condensed with cooling water at 20 °C and the liquid fraction was separated from the gases in another separator. Each product was further analysed.

Analysis of products. In the present work the change of product properties was studied as function of cracking parameters. Gas and liquid products formed in cracking reactions were analyzed using the following methods:

- classical determination of olefin content with iodine-bromine I/Br number (ASTM-D 149-60),
- liquid density measurement (MSZ EN ISO 12185),
- determination of Engler distillation curve (ASTM-D 1078),
- determination of the -CH₂-/-CH₃ ratio in liquid fractions with IR spectroscopy,
- determination of the olefin double bond distribution with SHIMADZU IR-470 type spectrometer,
- gas analysis using a Carlo Erba Vega Series GC 6000 gas-chromatograph (GC) provided with a 50 m × 0.32 mm fused silica column with Al₂O₃/KCl coating, at 40 °C,
- liquid analysis using a TRACE GC gas-chromatograph provided with a 30m x 0.32mm Rtx[®]-1 (Crossbond[®] 100% Dimethyl-polysiloxane) column. The temperature program of analysis started at 40 °C (2 min.), then the temperature arising with 7°C/min. to 330°C,
- determination of sulfur and nitrogen content of liquids (ASTM D 6428 99).

Results and Discussion

Yields. The cracking behaviour of a waste polyethylene and polypropylene was investigated in a horizontal tube reactor at 525°C cracking temperature, using different residence time ($\tau = 0.6, 0.9, 1.2h$). In cracking reactions three different products were formed: gas, liquid and residue, which consist of hydrocarbon chains of different length. The yields of formed products after cracking are shown in Figure 2. It was found, that the yields of volatile products are increased with residence time in case of both polymers. This might be due to the thermal stability of carbon chain. At a residence time 1.2h the melted polymer was for a longer time under the thermal degradation effect. It is well known, that the number of the cracking of the

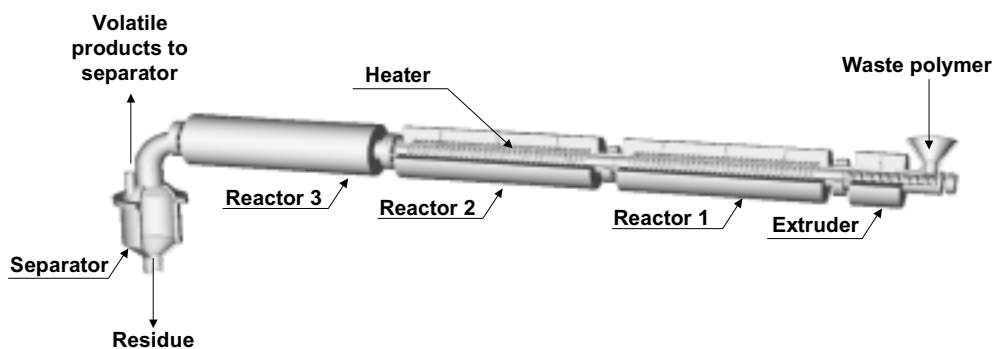


Figure 1. Cracking apparatus for cracking of waste polyolefins

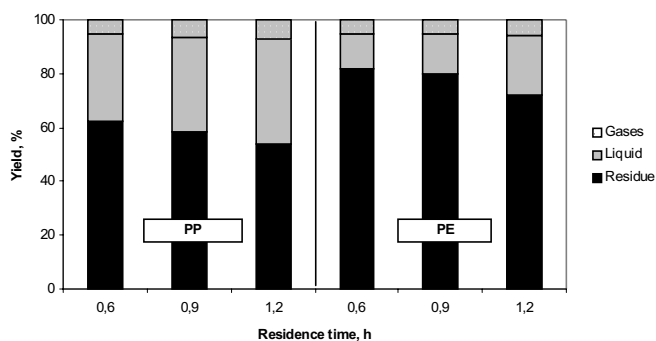


Figure 2. The yields of products in the cracking process

carbon chain increase with increasing the time of thermal effect, therefore forcible degradation conditions result lighter hydrocarbons with shorter carbon chain. It could cause the growing amount of the volatile products. From the wastes in case of PP could be observed higher yield of liquids (32.7, 35.5, 38.2%) in contrast to the PE waste (12.4, 15.1, 21.9%, resp.).

This fact can be explained by the difference in activation energy of two polymers. PP has lower activation energy than PE, because carbon chain of PP polymer contains tertiary carbon atoms, which have considerably lower resistance against degradation. Therefore at the same circumstance (cracking temperature, residence time etc.) the PP can be degraded easier than PE, therefore the cracking of PP could result higher amount of liquids and gases.

Structure of products. Gases. According to previous papers [14-18] the gas composition did not change with cracking temperature at mild cracking conditions. The change of composition of gases with different residence time is compared in Figures 3-4. Differences are not observed between various gas compositions obtained with different residence time, but the chemical structure of waste polymers significantly affected this property. Gases formed in the degradation of PP contained high amounts of C₃ hydrocarbons (propane and propene), in contrast to PE waste, where the C₂ and C₄ compounds were the main fractions.

The chemical structure of raw materials been blamed for this phenomenon too. It is known that the thermal degradation of polymers take place by radical mechanism and results mainly in monomers and oligomers. PP has branched carbon chain from monomers of three carbon atoms (propylene), but the car-

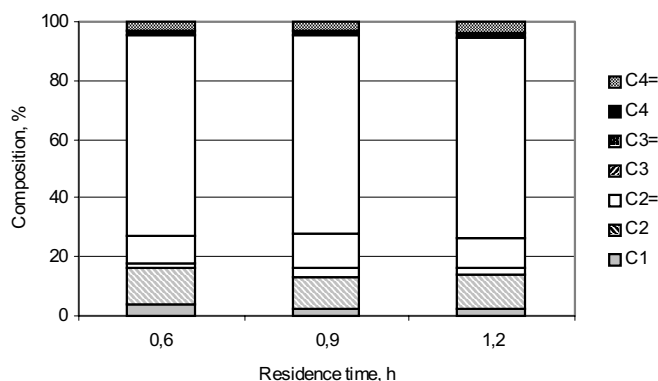


Figure 3. The composition of gases after cracking of PP waste

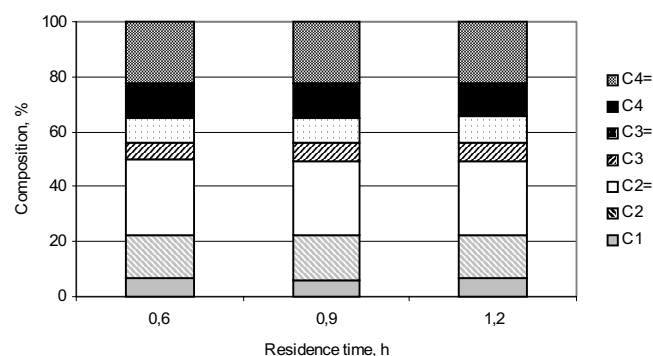


Figure 4. The composition of gases after cracking of PE waste

bon chain of PE built up from monomers of two carbon atoms (ethylene). The carbon chain of PP cracked in highest likelihood in the ramification of its, because the tertiary carbonium ion has the lowest thermal stability, therefore was mainly propylene in gases. On the other hand polyethylene consists of $-(CH_2-CH_2)-$ monomers, which cracked into statistically determined fragments, e.g. ethane, ethane or butane, butane. The possible scheme of the degradation is shown in Figure 5.

Liquid fractions. The liquids formed in the condensation steps of the degradation process were analyzed by TRACE GC. The used column was a 30m x 0.32mm, coated with dimethylpolysiloxane. This apparatus under the applied circumstances separated the hydrocarbons according to polarity. Typical gas-chromatograms of liquid fractions are shown in Figs 5, 6. In case of PE the cracking of the carbon chain were determined only statistically, because it has not distinguished part, where

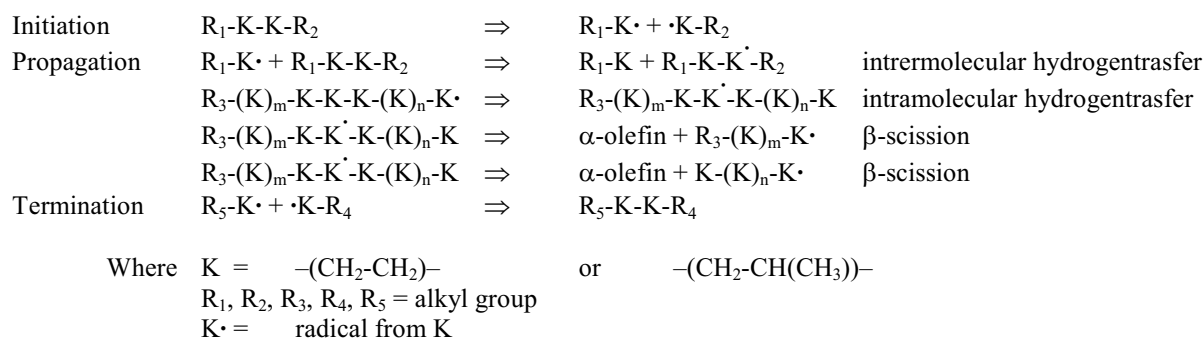


Figure 5. The scheme of cracking of polyolefin wastes

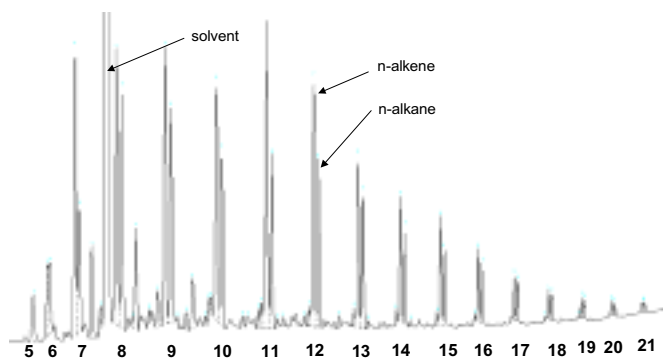


Figure 5. The gas chromatogram of liquid formed after the cracking of PE waste

the stability opposite to the thermal degradation might be lower than the other part of the carbon chain. Therefore fragments (n-alkane and n-alkene) arise from C_5 to C_{21} in all carbon numbers. In the gas chromatogram of liquid fraction formed after the cracking of PE waste there are doublets for each carbon number, one peak represents a n-olefin and the other a n-paraffin with the same carbon atom number.

According to Figure 5 the thermal cracking of PE produced hydrocarbons with mainly straight carbon chain. The main difference in the cracking of PP was the branched carbon chain of the polymer containing $-CH_3$ groups. Therefore cracking of PP resulted in fractions containing components with three carbon atoms sequences (C_6 , C_9 , C_{12} , C_{15} etc.). Naturally components with other carbon numbers were obtained as well but in the products, but these represented far lower concentrations. The gas chromatogram of liquids formed in the cracking of PP waste consists of no doublets but more splitted peaks of a given carbon numbers. I.e. wide distribution of isomer compounds is formed.

The composition of liquids has some differences as function of raw materials and residence time (Figures 7, 8). The residence time of the polymers affected the carbon atom distribution of products. In case of both polymers the liquid products became lighter with increasing residence time, the concentration of C_{10} -hydrocarbons is increasing, while the concentration of C_{10}^+ hydrocarbons when the residence time is increased from 0.6 to 1.2h is decreasing. At higher residence time the carbon chain was exposure more forceful thermal degradation effect, because

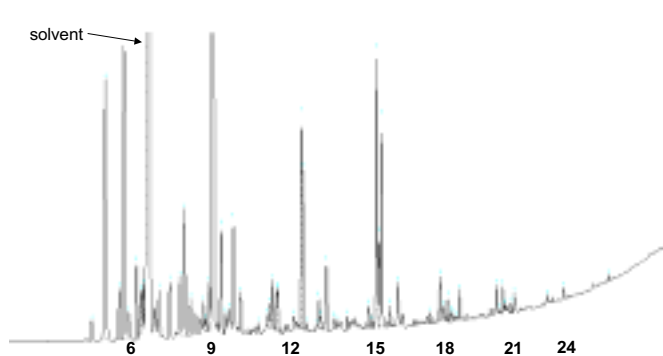


Figure 6. The gas chromatogram of liquid formed after the cracking of PP waste

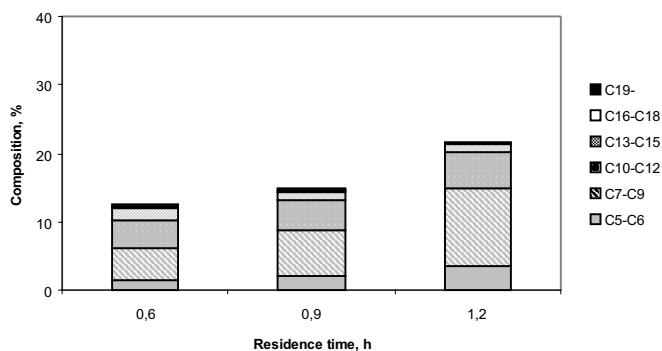


Figure 7. The yields of composition of liquid fractions obtained by cracking of PE

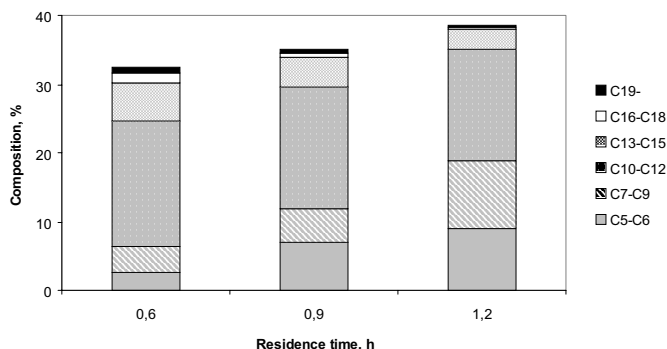


Figure 8. The yields of composition of liquid fractions obtained by cracking of PP

it was longer time in the reactor. This fact could occur the change of the distribution of the hydrocarbons.

The average molecular weight of the liquid fractions was calculated from the distribution of the carbon number of components in the liquids (Figure 9). Both the chemical type of the waste polymers and cracking parameter had an effect on the molecular weight.

The olefin content and its structure distribution of the liquid fractions are also very important properties for their potential use. The olefin concentration of liquid fractions and the distribution of double bonds were measured with the determination of I/Br number and measured by infrared technique. The I/Br numbers is shown in Figure 10. The residence time affected neither the olefin content nor the distribution of the olefins.

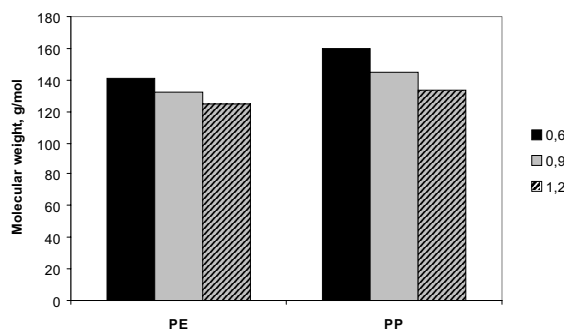


Figure 9. The average molecular weight of liquids at different residence time

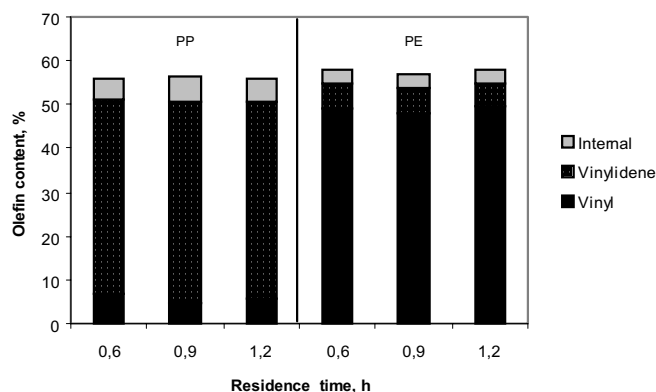


Figure 10. The olefin double bond distribution of liquid fractions

Higher olefin content could be observed in the liquid fractions produced by cracking of PP. It was found that the chemical type of the raw material has a significant effect not only on the yields, but on the distribution of the olefin double bonds, as well. The concentration of α -olefins was significant in case of each polymer, but the ratio of the vinyl and vinylidene bonds considerably depends on the type of the feed polymers.

The vinyl double bonds have two significant IR adsorption band at 910 and 990 cm^{-1} while vinylidene and internal type double bonds have peaks at 890 and 956 cm^{-1} , resp. As Fig. 11 shows some differences could be observed between the two types of polymer. The analysis of liquid products after degradation gave intensive adsorption band at 720 cm^{-1} , which is proportional to the length of the carbon chain ($n > 3$). The most intensive band were found in case of PE, because it has rather straight carbon chain, which was exempt from ramification. The main differences were observed in the olefin $=\text{CH}$ deformation vibrations. In the $\text{R}-\text{CH}=\text{CH}_2$ compounds the vinyl group has

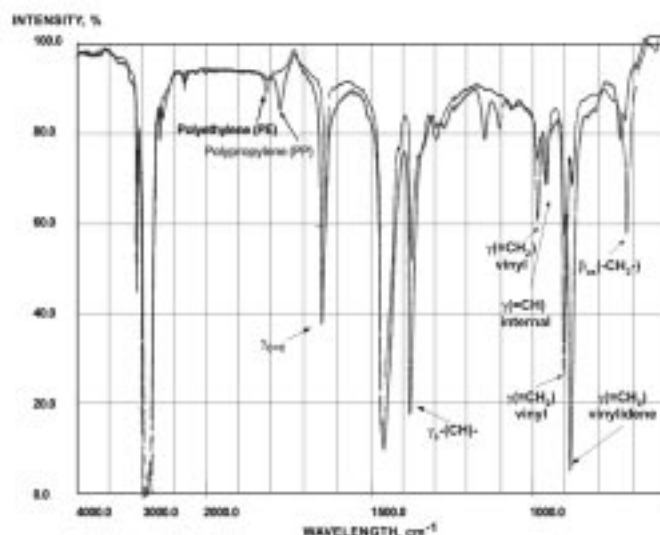


Figure 11. The IR spectra of liquids

a significant adsorption band at 910 and 990 cm^{-1} , which were more intensive in case of PE, and less notable in PP. The significant adsorption band from the deformation vibration of the vinylidene group in $\text{RR}'\text{C}=\text{CH}_2$ compounds at 890 cm^{-1} was more intensive in case of PP and less in case of PE.

The liquid fraction and residues obtained in the cracking reactions were measured and analyzed also as fuel like products. For the sake of investigation of this possibility, after thermal degradation the liquid products from the waste polymers and their residue were mixed and handled together. These mixtures were further separated with atmospheric and vacuum distillation into three fractions: white spirit like F1, diesel like F2 fractions and residue (F3). Table 3 represents the properties of each fraction in case of PP and PE wastes.

Table 3. The properties of fractions after distillation

Fraction	PP			PE		
	F1	F2	F3	F1	F2	F3
Yield ⁽¹⁾	19.9	25.3	48.5	9.5	29.0	56.4
Density, g/cm^3	0.748	0.809	-	0.718	0.795	-
Composition						
C ₅ -C ₆	18.9	0.0	-	25.3	0.0	-
C ₇ -C ₉	64.3	6.0	-	73.0	3.5	-
C ₁₀ -C ₁₂	18.6	13.1	-	1.7	20.3	-
C ₁₃ -C ₁₅	7.2	45.3	-	0.0	30.6	-
C ₁₆ -C ₁₈	0.5	16.9	-	0.0	32.4	-
C ₁₉ -C ₂₁	0.5	9.4	-	0.0	8.3	-
C ₂₂ -C ₂₄	0.0	5.8	-	0.0	4.5	-
C ₂₅ -C ₂₇	0.0	3.5	-	0.0	0.5	-
Groups in average molecule						
- CH ₂ -	6.4	10.0	-	7.6	15.0	-
- CH ₃	5.1	6.0	-	2.0	2.0	-
Olefin content						
Vinyl	3.5	5.5	-	46.9	39.1	-
Vinylidene	55.1	34.5	-	4.5	2.9	-
Internal	3.0	6.3	-	3.7	3.0	-
VK ₄₀ , $\text{m m}^2/\text{s}$	-	4.9	-	-	4.5	-
VK ₁₀₀ , $\text{m m}^2/\text{s}$	-	-	11.9	-	10.7	13.3
Pour point, °C	Under -50	-13	-	-41	-17	-
Flash point, °C	-	77	239	-	98	229
Corrosion test	Group 1.	Group 1.	-	Group 1.	Group 1.	-
S content, ppm	12	43	-	15	23	-
N content, ppm	3	4	-	7	12	-
Boiling range, °C	39-209	181-309	-	41-201	179-307	-
M, g/mol	105	211	-	107	213	-

⁽¹⁾ The yield applies to the weight of the raw material

The yield of the lighter liquid fractions (F1, F2) was 15-45% obtained in the cracking process (Figure 3). Some differences were observed between the characteristics of the two fractions (white spirit like F1 and diesel like F2). Thus F1 consists mainly lighter hydrocarbons C_5 - C_{12} and the F2 C_{13+} . The chemical structure of waste polymers affected the composition of each fraction. In case of PP the F1 fraction contains a significant amount of components C_5 - C_6 besides C_7 - C_9 content in case of the PE, the same fraction has rather C_7 - C_9 and C_{10} - C_{12} content. Nevertheless the PP degradation has higher yields in the F1 and F2 fractions. On the other hand residue of PP cracking products was softer consistence than PE cracking.

The number of $-CH_2-$ and $-CH_3$ groups were determined by IR technique in the range of 2800 - 3100cm^{-1} , i.e., in the C-H stretching vibration range of hydrocarbons. The number of the $-CH_2-$ groups is proportional to the intensity of asymmetric stretching vibration band at 2927cm^{-1} and the number of the $-CH_3$ groups to that of asymmetric stretching vibration band at 2958cm^{-1} . The change of $-CH_2-$ and $-CH_3$ groups in the liquid phase fraction molecules is shown in Table 2. It was found, that PP waste degradation products have significantly higher $-CH_3$ content, because of the chemical structure of PP. The F1 fraction of PP has higher sum of the carbon atoms of $-CH_2-$ and $-CH_3$ groups were, too, as the average molecular weight shows. From the other hand, the pour point of F1 from PP was lower than that of F1 from PE, because of ramification. The flash point of PP cracking products was lower too, because branched molecules have lower boiling point and greater volatility.

Also the F1 fractions have higher olefin content than F2 fractions. It is remarkable, because one possible way of the utilization of these products is the use as fuels. F2 is a diesel like liquid, which need rather saturated hydrocarbons, than olefins.

Each F2 fraction has higher sulfur and nitrogen content, than the F1 fractions. It was supposed, that polymers containing heteroatoms with additives (flame-retardant, antismoke additive) were degraded, the volatile decomposition products with sulfur and nitrogen content condensed in the fraction of heavier hydrocarbons.

Conclusions

The degradation of a waste polyethylene and polypropylene was investigated in a horizontal tube reactor. The yields and the structure of the products were determined. It was found that the cracking parameters – both the chemical type of wastes and residence time of cracking – have a significant effect both on the yields and structure of products. Higher yields of volatile products were observed in case of PP waste and longer residence time. Mainly propane and propene arose in cracking reactions of PP while C_2 and C_4 hydrocarbons formed in case of PE. In liquids branched hydrocarbons were observed in case of PP and aliphatic compounds in cracking of PE. By distillation further valuable liquid products could be separated from the residues. These products had favorable properties for fuel like application.

Acknowledgement

The authors are grateful to the Chemical Engineering Institute's Cooperative Research Center for financial support received

for this work. They would also like to thank Gabor Nagy and Zsolt Szoboszlai for technical help.

References

- [1] APME, "Summary Report: An analysis of plastics consumption and recovery in Western Europe 1999", Brussels, 2001
- [2] Aguado, J.; Serrano, D. P.: Feedstock Recycling of Plastic Wastes (J. H. Clark ed.), RSC, Cambridge, 1999
- [3] Sartorius I.: Development Plastics Manufacturing Industry in Europe, ICS-UNIDO Conference, Trieste, 2002, September, Italy
- [4] DEFRA: „Waste Strategy 2000: England and Wales Part II, Chap. 5, 64-88, 2000
- [5] Joseph, P.V.; Marcelo S.; Rabello, L.H.; Mattuso, C.: Environmental effects on the degradation behavior of sisal fibre reinforced polypropylene composite, Composites Science and Technology 62, 2002, 1357-1372.
- [6] Manchadó, M. L.; Torre, L.; Losé M. K.: Kinetic analysis of the thermal degradation of PP-EPDM blends, Rubber Chemistry and Technology 23, 2002, 73-84.
- [7] Ballice, L.; Reimert, R.: Classification of volatile products from the temperature-programmed pyrolysis of polypropylene (PP), atactic-polypropylene (APP) and thermogravimetrically derived kinetics of pyrolysis, Chemical Engineering and Processing 41, 2002, 289-296.
- [8] Hwang, E. Y.; Kim, J. R.; Chio, J. K.: Performance of acid treated natural zeolites in catalytic degradation of polypropylene, Journal of Analytical and Applied Pyrolysis, 62, 2002, 351-364.
- [9] Manos, G.; Garforth, A.; Dwyer, J.: Catalytic degradation of high-density polyethylene over different zeolitic structures, Ind. Eng. Chem. Res. 39, 2000, 1198-1214
- [10] Schirmer, J.; Kim, J. S.; Klemm, E.: Catalytic degradation of polyethylene using thermal gravimetric analysis and a cycled-spheres-reactor, Journal of Analytical and Applied Pyrolysis 60, 2001, 205-215
- [11] Kim, J. R.; Kim, Y. A.; Yoon, J. H.; D. Park, W.; Woo, H. C.: Catalytic degradation of polypropylene: effect of dealumination of clinoptilolite catalyst, Polymer Degradation and Stability, 75, 2002, 287-294.
- [12] Kim, J. R.; Kim, Y. A.; Yoon, J. H.; D. Park, W.; Woo, H. C.: Catalytic recycling of the mixture of polypropylene and polystyrene, Polymer Degradation and Stability, 76, 2002, 61-67.
- [13] Lin Y. H., Sharratt P. N.: Conversion of waste plastics to hydrocarbons by catalytic zeolited pyrolysis, Journal of the Chinese Institute of Environmental Engineering, 10, 2000, 271-277
- [14] Chirico, A. D.; Armanini, M.; Chini, P.; Cioccolo, G.; Provasoli, F.; Audisio, G.: Flame retardants for polypropylene based on lignin, Polymer Degradation and Stability, 79, 2002, 139-145.
- [15] Jayaraman, J.: Manufacturing sisal-polypropylene composites with minimum fibre degradation, Composites Science and Technology 63, 2003, 367-374.
- [16] Kim, H.; Lee, J. W.: Effect of ultrasonic wave on the degradation of polypropylene melt and morphology of its blend with polystyrene, Polymer 43, 2002, 2585-2589.
- [17] Miskolczi, N.; Bartha, L.; Deák, Gy.; Jóvér, B.; Kalló, D.: Investigation of hydrocarbon mixtures obtained from waste polymer degradation, MODEST, Budapest, 2002, July, Hungary
- [18] Miskolczi, N.; Bartha, L.; Deák, Gy.; Jóvér, B.; Kalló, D.: Investigation of Thermal and Catalytic Cracking of Waste Polyethylene, Hungarian Chemistry Journal, 2003, 5, 172-177