

PYROLYSIS OF HIGH DENSITY POLYETHYLENE (HDPE) IN THE OPEN SYSTEM

I. Kojć¹, A. Bechtel², S. Trifunović¹, K. Stojanović¹

¹University of Belgrade, Serbia, ²Montanuniversität Leoben, Austria

Conversion of polymeric materials into useful products has been attaining recognition in recent years. Pyrolysis of high density polyethylene (HDPE) in the open system was examined. Plastic bag for food packing was used as a source of HDPE. Pyrolysis of HDPE was performed in open system (Pyrolyser, Model MTF 10/15/130 Carbolite, UK) under a nitrogen atmosphere during 4 hours at three temperatures 400, 450 and 500 °C. The temperature range between 400 °C and 500 °C was chosen, concerning the thermogravimetric properties of HDPE (Ray, Cooney, 2012). Liquid pyrolysis products were extracted using hot chloroform. The solid residue was dried and weighed, whereas yield of gas was calculated as: 100 % – (yield of liquid pyrolysate + yield of solid residue). Solid residue was characterized by elemental analysis, whereas liquid products were analyzed by gas chromatography-mass spectrometry.

As expected, increase of the temperature from 400 °C to 500 °C resulted in increase of conversion of HDPE into liquid and gaseous products (Table 1).

The main constituents of all liquid pyrolysates are *n*-alkanes and terminal *n*-alkenes. *n*-Alkanes are identified in range from C₁₃ to C₃₇. *n*-Alkane patterns of all samples showed equal abundance of odd and even numbered homologues. Liquid pyrolysate obtained at 400 °C is characterized by prevalence of long-chain homologues having *n*-alkane maximum in the range C₃₂ to C₃₆. On the other hand, pyrolysates obtained at 450 °C and 500 °C displayed *n*-alkane distributions similar to those typical for saturated fraction of oil, with *n*-alkane maximum at C₁₇-C₁₈ and C₁₆-C₁₇, respectively. Proportion of short-chain (C₁₄-C₂₀) increased, whereas proportion of long-chain (C₂₆-C₃₇) *n*-alkanes decreased with temperature rise from 400 °C to 500 °C. Proportion of middle-chain (C₂₁-C₂₅) *n*-alkanes showed the following trend 450 °C > 500 °C > 400 °C (Table 1). Terminal *n*-alkenes were identified in range from C₁₃ to C₃₁, with equal abundance of odd and even homologues. Pyrolysate obtained at 400 °C showed maxima in range C₂₈-C₃₀. In pyrolysates obtained at 450 °C and 500 °C the most prominent *n*-alkene homologues were C₁₈-C₁₉ and C₁₇-C₁₈, respectively. Proportion of short-chain (C₁₄-C₂₀) *n*-alkenes increased, whereas proportion of long-chain (C₂₆-C₃₁) *n*-alkenes decreased with temperature rise. Proportion of middle-chain (C₂₁-C₂₅) *n*-alkenes showed the following trend: 450 °C > 400 °C > 500 °C (Table 1). *n*-Alkylcyclohexanes ranged from C₁₄ to C₂₆ (total number of carbon atoms) were present in all samples, with no odd/even predominance. C₂₀-C₂₁ *n*-alkylcyclohexanes are the most abundant in pyrolysate at 400 °C, whereas pyrolysates at 450 °C and 500 °C are characterized by the prevalence of C₁₈ and C₁₆ homologues. Proportion of short-chain (C₁₄-C₁₈) *n*-alkylcyclohexanes increased with temperature rise, while proportions of middle-chain (C₁₉-C₂₃) and long-chain (C₂₄-C₂₆) homologues showed the opposite trend (Table 1). Liquid pyrolysates contained very low amount of aromatic hydrocarbons. *n*-Alkylbenzenes and *n*-alkyltoluenes (in traces) represent exclusive aromatics identified in HDPE pyrolysates, most probably formed via dehydrocyclization of reactive radicals. *n*-Alkylbenzenes were identified in the same range as *n*-alkanes, C₁₄-C₃₇, with no odd/even predominance. Pyrolysate obtained at 400 °C showed *n*-alkylbenzene maximum in range C₂₁-C₂₃, whereas pyrolysates at 450 °C and 500 °C are characterized by prevalence of C₁₇ and C₁₈ or C₁₆ and C₁₈, respectively. Differences in hydrocarbons distributions were more pronounced between pyrolysates obtained at 400 °C

and 450 °C, than between liquid products at 450 °C and 500 °C, consistent with thermogravimetric properties of HDPE. Concerning the temperature rise from 450 °C to 500 °C more intense changes were observed in distributions of *n*-alkenes and *n*-alkylcyclohexanes than for *n*-alkanes and particularly *n*-alkylbenzenes (Table 1). Important characteristic of liquid pyrolysates is very low content of aromatic hydrocarbons in comparison to crude oils.

Contents of carbon, hydrogen and oxygen in the solid residues were in range from 83.75 % to 84.54 %, from 13.30 % to 13.35 %, and from 2.12 % to 2.95 %, respectively, indicating molecular formulas CH_{1.906}O_{0.026} at 400 °C, CH_{1.893}O_{0.019} at 450 °C and CH_{1.898}O_{0.020} at 500 °C, which are slightly depleted in hydrogen than theoretical formula of HDPE, CH₂. Average calculated net calorific value of solid residues based on five formulas with standard deviation of 0.92 – 0.94 MJ/kg (https://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/25_3_SAN%20FRANCISCO_08-80_0235.pdf) ranged from 43.13 MJ/kg to 43.57 MJ/kg, which is higher than those of subbituminous coal and petroleum coke. In addition these solid residues do not contain sulphur and do not produce ash by combustion.

The results of this study indicate that open system pyrolysis of HDPE, at temperatures between 450 °C and 500 °C seems to be an attractive way for its transformation into valuable liquid and solid products.

Table 1. Yields of the pyrolysis products and distributions of hydrocarbons in liquid pyrolysates

Yields of the pyrolysis products	Temperature	Solid residue (%)	Liquid (%)	Gas (%)
	400 °C	79.63	12.96	7.41
	450 °C	67.17	21.32	11.51
	500 °C	50.29	33.94	15.77
Relative proportions of <i>n</i> -alkanes	Temperature	C ₂₆ -C ₃₇ (%)	C ₂₁ -C ₂₅ (%)	C ₁₄ -C ₂₀ (%)
	400 °C	65.60	17.94	16.46
	450 °C	40.41	25.20	34.39
	500 °C	37.92	21.85	40.23
Relative proportions of <i>n</i> -alkenes	Temperature	C ₂₆ -C ₃₁ (%)	C ₂₁ -C ₂₅ (%)	C ₁₄ -C ₂₀ (%)
	400 °C	43.82	30.46	25.72
	450 °C	32.03	31.88	36.09
	500 °C	25.22	27.91	46.88
Relative proportions of <i>n</i> -alkylcyclohexanes	Temperature	C ₂₄ -C ₂₆ (%)	C ₁₉ -C ₂₃ (%)	C ₁₄ -C ₁₈ (%)
	400 °C	24.32	45.97	29.71
	450 °C	17.56	39.91	42.53
	500 °C	11.61	34.56	53.83
Relative proportions of <i>n</i> -alkylbenzenes	Temperature	C ₂₆ -C ₃₇ (%)	C ₂₁ -C ₂₅ (%)	C ₁₄ -C ₂₀ (%)
	400 °C	39.89	30.91	29.20
	450 °C	30.80	27.09	42.11
	500 °C	35.47	22.36	42.18

References

- Ray, S., Cooney, R.P., 2012. Thermal Degradation of Polymer and Polymer Composites. In Kutz, M. (Ed.), Handbook of Environmental Degradation of Materials, Second Edition. Elsevier Inc., Oxford, pp. 213-242.
https://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/25_3_SAN%20FRANCISCO_08-80_0235.pdf (last accessed January 19, 2017).