CHEMISTRY & CHEMICAL TECHNOLOGY

Chem. Chem. Technol., 2023,
Vol. 17, No. 4, pp. 923–928

Chemical Technology

STUDY ON REGULARITIES OF POLYETHYLENE WASTE LOW-TEMPERATURE PYROLYSIS

***Ksenia Hrynyshyn*[1], *Taras Chervinskyy*[1,✉], *Igor Helzhynskyy*[1], *Volodymyr Skorokhoda*[1]**

https://doi.org/10.23939/chcht17.04.923

Abstract. A low-temperature pyrolysis with pyrocondensate as a target product is one of the options for processing polyethylene waste. The fractional composition and properties of the pyrocondensate obtained at different temperatures and times were studied. Pyrocondensate was separated into gasoline, diesel fractions, and the residue. The composition and properties of mentioned fractions were established and related to the conditions of the pyrolysis process. X-ray fluorescence analysis of pyrocondensate and narrow fractions isolated from it was carried out.

Keywords: polyethylene waste, utilization, pyrolysis, pyrocondensate, X-ray fluorescence analysis, motor fuels.

1. Introduction

One of the most important environmental problems of our time is the processing of polymer waste, which is accumulated on an extremely large scale and poses a threat to the environment.[1,2] Polymer waste is accumulated in landfills, scattered in forests and fields, and floats on almost all water surfaces of our planet, polluting the environment. And given the fact that polymeric waste practically does not decompose, its amount is increasing every day.[3,4] This problem has already become a global issue. Among the known methods of polymer waste disposal are incineration, recycling, and reuse, but the method of low-temperature pyrolysis of polymer waste deserves special attention, as it allows to fully utilize the peculiarities of their chemical structure.[5-8]

The pyrolysis process is widely used in the oil refining and petrochemical industries to produce ethylene hydrocarbons. When hydrocarbons are pyrolyzed to ethylene and propylene, the main liquid by-products are pyrocondensate and heavy resin, with yields ranging from 25–30 %.[9] Petroleum polymer resins are obtained from narrow fractions of pyrocondensate,[10-13] which are used as components of various composite materials and effective modifiers of petroleum bitumen.[14,15]

The known process of low-temperature pyrolysis of rubber waste is carried out at batch plants at temperatures of 450-500°C.[16] This process produces a liquid product – pyrocondensate, pyrolysis gas, and a solid residue – pyrocarbon.[17] Pyrocondensate is mostly used as a furnace fuel, although it is advisable to separate it into narrow fractions and use it as a raw material for the production of commercial motor fuels.[18]

Pyrolysis of polymer waste is also used in industry.[19-23] However, the bulk of research on this process is related to the processing of unsorted waste, which greatly complicates the perception and understanding of the basic laws of this process. An important aspect is also the study of the influence of the pyrolysis process technological parameters on the yield and composition of the main product – pyrocondensate.

The aim of this work was to study the yield, composition, and properties of pyrocondensate, obtained during the polyethylene waste pyrolysis, depending on the pyrolysis process mode.

2. Experimental

The starting material was polyethylene waste, namely the segments obtained as a result of the formation of polyethylene products.

The process of polyethylene waste pyrolysis was carried out on a laboratory setup, which consisted of a hermetic metal reactor, an electric heater, a water cooler, and a receiver. Pre-weighed polyethylene waste was loaded into the reactor. The setup was assembled, the electric heater was turned on and the temperature was brought to the operating temperature required for the pyrolysis process. The temperature was measured using a thermocouple. Vapors formed during pyrolysis were cooled and partially condensed in a water cooler. The non-condensed part of the products (pyrogases) was released into the atmosphere. The condensed part of the products (pyrocondensate) was collected using a receiver. After

[1] Lviv Polytechnic National University
12, S. Bandery St., Lviv, 79013, Ukraine
✉ *chervinskijt@gmail.com*

pyrolysis, the unit was disassembled, the reactor and receiver were weighed, and the amount of pyrocondensate and residue was determined. After that, the material balance of the process was drawn up.

The process of pyrocondensate separation (distillation) into narrow fractions was carried out on a classic laboratory setup for the separation of light petroleum products. The setup consists of a flask, a flask heater, a water cooler, a prolong, and a receiver for collecting narrow fractions. The temperature of fractions selection was fixed with the help of a thermometer, which was used to measure the temperature of the vapors at the entrance to the refrigerator.

Determination of the composition and properties of pyrocondensate and narrow fractions separated from it was carried out according to the generally accepted methods.[24] In particular, the fractional composition of light fractions was determined on the apparatus for the distillation of light petroleum products; the flash point was determined in a closed cup for light fractions, and in an open cup for heavy fractions. The density of pyrocondensate and fractions separated from it was determined by the pycnometric method; the iodine number of all fractions was determined by the Margoshes method.

X-ray fluorescence spectral analysis was used to determine the content of individual chemical elements in the pyrocondensate and the fractions separated from it. The analysis was performed on a precision Elvax Light SDD analyzer.

3. Results and Discussion

The process of polyethylene waste pyrolysis was carried out in three heating modes, which were characterized by different process temperatures and times. Fig. 1 shows the characteristics of three modes under study. Dots on the curves show the moment of the process start and end. Mode 1 is characterized by a minimum temperature (400 ºC), but a maximum time (65 min). Instead, Mode 3 is characterized by maximum rigidity – the process temperature is 450 ºC and the minimum time (28 min).

The yield of pyrocondensate was 81.4–89.3 wt. % relative to the raw material and depends on the process mode. The material balance of the process is given in Table 1. It was found that the increase in the process rigidity (increase in the process temperature) decreases the yield of pyrocondensate and increases the yields of pyrolysis gases and residue.

For the obtained pyrocondensate, the main quality indices and fractional composition were determined according to the standardized method. The results of the research are given in Table 2 and Fig. 2.

It was established (Table 2) that pyrocondensate contains a significant amount of unsaturated hydrocarbons, which is confirmed by the high iodine number. The freezing point of pyrocondensate (5–18 ºC) indicates a high content of paraffin hydrocarbons in it. There is no sulfur in pyrocondensate, which is explained by the absence of sulfur in the pyrolysis feedstock. It was established that at high pyrolysis temperatures, pyrocondensate with a lower freezing point and a higher content of unsaturated hydrocarbons is formed. The initial boiling temperature (IBP) of pyrocondensate is somewhat higher compared to oil and depends on the process mode (Fig. 2): the higher the pyrolysis temperature, the lower the IBP of pyrocondensate.

It was found (Fig. 2) that the pyrolysis process mode significantly affects the fractional composition of pyrocondensate. The higher the pyrolysis temperature, the lighter the pyrocondensate fractional composition (higher content of fractions boiled up to 350 ºC). This feature is very important precisely for obtaining components of motor fuels from pyrocondensate.

The pyrocondensate obtained by the polyethylene waste pyrolysis was separated into individual fractions and their composition and properties were studied with the aim of further use for the production of commercial motor fuels. When separating the pyrocondensate we obtained the fraction IBP-200 ºC), the fraction 200–350 ºC, and the residue, the characteristics of which are given in Tables 3-5.

Table 1. Material balance of polyethylene waste pyrolysis

Feed and products	Amount, wt. %		
	Mode 1	Mode 2	Mode 3
Feed: Polyethylene waste	 100.0	 100.0	 100.0
Products: Pyrocondensate Residue Gas and losses	 89.3 0.2 10.5	 87.8 0.3 11.9	 81.4 0.5 18.1
Total	100.0	100.0	100.0

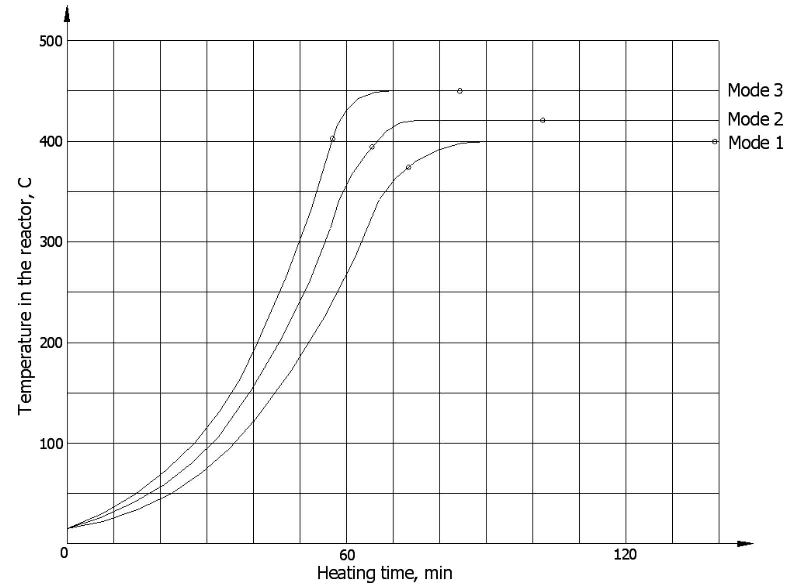

Fig. 1. Polyethylene waste pyrolysis modes

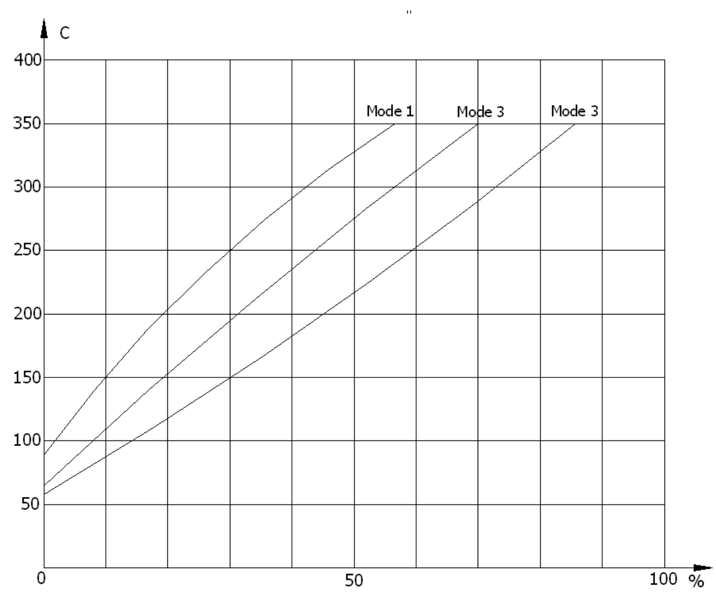

Fig. 2. Boiling point curves of pyrocondensate of polyethylene waste pyrolysis

Table 2. Properties of pyrocondensate of polyethylene waste pyrolysis

Index	Value		
	Mode 1	Mode 2	Mode 3
Density, g/cm^3	0.884	0.872	0.856
Refractive index	1.4276	1.4312	1.4365
Sulfur content, wt. %	absent	absent	absent
Iodine number, g I_2/100 g	73.1	78.4	85.9
Freezing point,°C	+18	+12	+5
Flash point open cup, °C closed cup, °C	 55 28	 51 24	 49 22

Table 3. Composition and characteristics of the IBP-200ºC fraction

Index	Value		
	Mode 1	Mode 2	Mode 3
Yield relative to pyrocondensate, wt. %	19.6	31.2	45.2
Yield relative to polyethylene, wt. %	17.5	27.4	36.8
Density, g/cm^3	0.773	0.782	0.795
Refractive index	1.4017	1.4127	1.4260
Fractional composition IBP, °C 10 % distilled, b.p., °C 50 % distilled, b.p., °C 90 % distilled, b.p., °C EBP, °C	 52 72 124 188 201	 52 76 127 190 203	 54 78 129 193 206
Sulfur content, wt. %	absent	absent	absent
Iodine number, g I_2/100 g	88.9	91.4	95.1

Table 4. Composition and characteristics of the 200-350ºC fraction

Index	Value		
	Mode 1	Mode 2	Mode 3
Yield relative to pyrocondensate, wt. %	36.9	38.7	40.6
Yield relative to polyethylene, wt. %	33.0	34.0	33.0
Density, g/cm^3	0.854	0.868	0.875
Refractive index	1.4228	1.4278	1.4315
Iodine number, g I_2/100 g	78.4	80.6	83.2
Fractional composition IBP, °C 10 % distilled, b.p., °C 50 % distilled, b.p., °C 90 % distilled, b.p., °C 98 % distilled, b.p. °C	 195 210 261 338 352	 197 214 267 340 354	 198 217 272 343 358
Sulfur content, wt. %	absent	absent	absent
Cloud point, °C	1	0	–1
Freezing point, °C	–6	–8	–10
Flash point in closed cup, °C	60	62	65

The IBP-200 ºC fraction isolated from pyrocondensate is a transparent colorless liquid with a characteristic smell. The fraction is characterized by a heavier fractional composition, compared to straight-run gasoline obtained from oil, and by the complete absence of sulfur (Table 3). The presence of unsaturated hydrocarbons is confirmed by high values of iodine numbers. When the rigidity of the pyrolysis mode increases, the fractional composition becomes heavier, and the density and content of unsaturated hydrocarbons increase. In terms of fractional composition, this fraction is close to commercial motor gasoline. However, taking into account the high content of paraffin hydrocarbons in it, which is confirmed by the refractive index, it is characterized by a low octane number. In addition, the unsaturated hydrocarbons contained in the IBP-200 ºC fraction are undesirable components of motor fuels. Therefore, this fraction can be used as a component of commercial gasoline only after additional processing, which involves the hydrogenation of unsaturated hydrocarbons and an increase in the octane number.

The 200–350 ºC fraction isolated from pyrocondensate is a light yellow transparent liquid with a characteristic smell. In terms of density, sulfur content, and flash point in an open cup, this fraction meets the requirements for commercial diesel fuels (Table 4). However, during long-term storage, a small amount of paraffin hydrocarbons is precipitated, which is extremely undesirable. Similar to pyrocondensate and IBP-200ºC fraction, the fraction of 200–350 ºC contains unsaturated hydrocarbons, which is confirmed by the iodine number. The cloud and freezing points of the 200–350 ºC fraction obtained under rigid conditions (Mode 3) meets the requirements for commercial summer diesel fuels. Analogous fractions obtained under milder conditions have unsatisfactory low-temperature properties and require additional processing with the use of dewaxing or hydroisomerization. To obtain winter diesel fuels, all three investigated fractions of 200–350 ºC must be additionally processed to achieve a lower freezing point.

Table 5. Composition and characteristics of the residue >350ºC

Index	Value		
	Mode 1	Mode 2	Mode 3
Yield relative to pyrocondensate, wt. %	43.5	30.1	14.2
Yield relative to polyethylene, wt. %	38.8	26.4	11.6
Density, g/cm^3	0.921	0.932	0.944
Refractive index	1.4402	1.4514	1.4680
Sulfur content, wt. %	absent	absent	absent
Iodine number, g I_2/100 g	59.8	62.6	67.5
Freezing point, °C	45	42	41
Flash point open cup, °C closed cup, °C	 139 110	 132 106	 124 102
Penetration (cone), 0.1 mm	208	221	239

Table 6. Content of individual chemical elements in pyrocondensate and fractions isolated from it

Element	Element content, ppm			
	Pyrocondensate	IBP-200 °C fraction	200–350 °C fraction	Residue >350°C
Ca	15.3	8.2	9.3	17.8
V	0.1	0.1	0.1	0.2
Cr	1.9	1.7	1.9	2.3
Mn	0.1	0.1	0.1	0.1
Fe	3.0	0.7	2.8	5.4
Ni	0.1	0.1	0.1	0.1
Cu	12.4	12.0	12.4	14.6
Zn	1.0	0.3	1.1	2.4
Ba	0.1	0.1	0.1	0.1
Mo	5.9	2.8	4.4	7.1
Pb	1.0	1.0	1.0	1.0

The residue after pyrocondensate distillation is a light-yellow product that visually resembles plastic lubricant. It is characterized by a freezing point of 41–45 ºC (Table 5). When the rigidity of the pyrolysis process increases, the freezing point and flash point of the residue decrease but the content of unsaturated hydrocarbons increases. This product can be used as a component of fuel oil in small quantities or as a base for the production of plastic lubricants. However, this direction of application needs more detailed research.

The content of individual chemical elements in pyrocondensate and narrow fractions isolated from it was determined using X-ray fluorescence spectral analysis (Table 6).

No heavy metals characteristic of oil fractions and residues (V, Ni) were found in the pyrocondensate and its fractions. Instead, Ca, Fe, Cu, and Mo were found. Moreover, the heavier the fraction, the higher the content of metals in it. However, the content of these metals is insignificant and cannot pose a threat during the processing of individual fractions at classic technological installations of oil refining.

A preliminary analysis of the results of determining the properties of narrow fractions isolated from pyrocondensate showed that they cannot be used as components of commercial oil fuels. These fractions must be pre-processed separately or mixed with the corresponding oil fractions, but the choice of their application requires further research.

4. Conclusions

1. The influence of the polyethylene waste pyrolysis process mode on the yield and composition of pyrocondensate was studied. It was found that the higher the pyrolysis temperature, the lower the yield of the liquid product – pyrocondensate. At higher temperatures, pyrocondensate of a lighter fractional composition is formed. In particular, at the pyrolysis temperature of 400 ºC, the content of light fractions in pyrocondensate is 56.5 wt.%, and at the temperature of 450 ºC – 85.8 wt.%.

2. The composition and properties of narrow fractions isolated from the pyrocondensate of polyethylene waste pyrolysis were studied. It was found that the gasoline fraction of IBP-200 ºC is characterized by a high content of unsaturated hydrocarbons (iodine number is 88.9-95.1 g I_2/100 g) and low octane number and requires further processing to hydrogenate unsaturated hydrocarbons and increase the octane number.

3. It has been established that the 200–350 ºC fraction of the pyrocondensate obtained at 450 ºC meets the requirements for summer diesel fuel in terms of the main indices. To obtain winter diesel fuel, it is necessary to additionally use special processes for the reduction of freezing point.

4. The residue of pyrocondensate distillation >350 ºC can be used as a component of fuel oil in small quantities or

as a basis for the production of plastic lubricants after additional research.

5. It was established that pyrocondensate and its fractions practically do not contain heavy metals characteristic of oil fractions and residues (V, Ni). Instead, Ca, Fe, Cu, and Mo were detected, but the content of these metals will not prevent the processing of individual fractions at classic oil refining technological units.

References

[1] Hamad, K.; Kaseem, M.; Deri, F. Recycling of Waste from Polymer Materials: An Overview of the Recent Works. *Polym. Degrad. Stab*. **2013**, *98*, 2801-2812. https://doi.org/10.1016/j.polymdegradstab.2013.09.025
[2] Ali, S.H.; Garforth, A.A.; Harris, D.H.; Rawlence, D.J.; Uemichi, Y. Polymer Waste Recycling Over "Used" Catalysts. *Catal. Today* **2002**, *75*, 247-255. https://doi.org/10.1016/S0920-5861(02)00076-7
[3] Sheldon, R.A.; Norton, M. Green Chemistry and the Plastic Pollution Challenge: Towards a Circular Economy. *Green Chem*. **2020**, *22*, 6310-6322. doi:https://doi.org/10.1039/D0GC02630A
[4] Su, L.; Xiong, X.; Zhang, Y.; Wu, C.; Xu, X.; Sun, C.; Shi, H. Global Transportation of Plastics and Microplastics: A Critical Review of Pathways and Influences. *Sci. Total Environ*. **2022**, *831*, 154884. https://doi.org/10.1016/j.scitotenv.2022.154884
[5] Datta, J.; Kopczyńska, P. From Polymer Waste to Potential Main Industrial Products: Actual State of Recycling and Recovering. *Crit. Rev. Environ. Sci. Technol*. **2016**, *46*, 905-946. https://doi.org/10.1080/10643389.2016.1180227
[6] Kemona, A.; Piotrowska, M. Polyurethane Recycling and Disposal: Methods and Prospects. *Polymers* **2020**, *2*, 1752. https://doi.org/10.3390/polym12081752
[7] Al-Maaded, M., Madi, N.K., Kahraman, R., Hodzic, A.; Ozerkan, N.G. An Overview of Solid Waste Management and Plastic Recycling in Qatar. *J. Polym. Environ*. **2012**, *20*,186-194. https://doi.org/10.1007/s10924-011-0332-2
[8] Panda, A.K.; Singh, R.K.; Mishra, D.K. Thermolysis of Waste Plastics to Liquid Fuel: A Suitable Method for Plastic Waste Management and Manufacture of Value Added Products—A World Prospective. *Renew. Sustain. Energy Rev*. **2010**, *14*, 233-248. https://doi.org/10.1016/j.rser.2009.07.005
[9] Bratychak, M.M.; Hrynyshyn, O.B.; Prysyazhnyy, Yu.V.; Pushak, A.P. *Naftopolimerni smoly iz funktsiy nymy hrupamy. Syntez vlastyvosti, zastosuvannya*; Publishing House of Lviv Polytechnic National University: Lviv, 2016.
[10] Bratychak, M.; Brostow, W.; Grynyshyn, O.; Shyshchak, O. Synthesis and Characterization of Petroleum Resins with Epoxy Groups. *Mater. Res. Innov*. **2003**, *7*, 167-171. https://doi.org/10.1007/s10019-003-0243-5
[11] Skibitskiy, V.; Grynyshyn, O.; Bratychak, M.; Waclawek, W. Obtaining of Petroleum Resins Using Pyrolysis By-Products. 4. Resins with Carboxy Groups. *Ecol. Chem. Eng*. **2004**, *11*, 41-51.
[12] Bratychak, M.; Grynyshyn, O.; Shyshchak, O.; Romashko, I.; Waclawek, W. Obtaining of Petroleum Resins Using Pyrolysis By-Products. 12. Petroleum Resins with Hydroxyl Groups. *Ecol. Chem. Eng*. **2007**, *14*, 225-234.
[13] Bratychak, M.; Shust, O.; Chervinskyy, T.; Shyshchak, O.; Waclawek, W. Obtaining of Petroleum Resins Using Pyrolysis By-Products. 14. Petroleum Resins with Fluorine Atoms. *Ecol. Chem. Eng*. **2011**, *18*, 49-54.
[14] Chervinskyy, T.; Bratychak, M.; Gagin, M.; Waclawek, W. Obtaining of Petroleum Resins Using Pyrolysis By-Products. 6. Petroleum Resins with Epoxy Groups as Active Components of Epoxy-Polymeric Composites. *Ecol. Chem. Eng*. **2004**, *11*, 1225-1231.
[15] Grynyshyn, O.; Bratychak, M.; Krynytskiy, V.; Donchak, V. Petroleum Resins for Bitumens Modification. Chem. Chem. Technol., 2008, 2, 47-53. http://dx.doi.org/10.23939/chcht02.01.047
[16] Pyshyev, S.; Lypko, Y.; Chervinskyy, T.; Fedevych, O.; Kułażyński, M.; Pstrowska, K. Application of Tyre Derived Pyrolysis Oil as a Fuel Component. *S. Afr. J. Chem. Eng*. **2023**, *43*, 342-347. https://doi.org/10.1016/j.sajce.2022.12.003
[17] Ryzhkov, S.; Rudyuk, N.; Markina, L. Research of Thermal Conductivity of the Condensed Mass of the Whole Waste Tires and Determination of their Optimum Arrangement in the Pyrolysis Reactor. *EasternEuropean J. Enterp. Technol*. **2016**, *82*, 12-18. http://dx.doi.org/10.15587/1729-4061.2016.73557
[18] Hrynyshyn, K.; Skorokhoda, V.; Chervinskyy, T. Study on the Composition and Properties of Pyrolysis Pyrocondensate of Used Tires. *Chem. Chem. Technol*. **2022**, *16*, 159-163. http://dx.doi.org/10.23939/chcht16.01.159
[19] Mikulionok, I. A State of Art and Prospects of Plastic Solid Waste Management. *Energy Technologies & Resource Saving* **2021**, *2*, 52-73. https://doi.org/10.33070/etars.2.2021.05
[20] Phakedi, D.; Ude, A.U.; Oladijo, P.O. Co-pyrolysis of Polymer Waste and Carbon-Based Matter as an Alternative for Waste Management in the Developing World. *J. Anal. Appl. Pyrolysis* **2021**, *155*, 105077. https://doi.org/10.1016/j.jaap.2021.105077
[21] Jung, S.; Choi, D.; Park, Y.-K.; Tsang, Y.F.; Klinghoffer, N.B.; Kim, K.-H.; Kwon, E.E. Functional Use of CO_2 for Environmentally Benign Production of Hydrogen Through Catalytic Pyrolysis of Polymeric Waste. *Chem. Eng. J*. **2020**, *399*, 125889. https://doi.org/10.1016/j.cej.2020.125889
[22] Srinivasan, S.; Valsadwala, A.S.; Begum, S.S.; Samui, A.B. Experimental Investigation on the Influence of Novel Catalyst in Co-Pyrolysis of Polymeric Waste: Characterization of Oil and Preparation of Char Reinforced Composites. *J. Clean. Prod*. **2021**, *316*, 128225. https://doi.org/10.1016/j.jclepro.2021.128225
[23] Zhang, L.; Bao, Z.; Xia, S.; Lu, Q.; Walters, K.B. Catalytic Pyrolysis of Biomass and Polymer Wastes. Catalysts 2018, 8, 659. https://doi.org/10.3390/catal8120659
[24] Topilnytskyy, P.; Grynyshyn, O.; Machynskyy, O. Tehnologia pervynnoi pererobky nafty i gazu. Publishing House of Lviv Polytechnic National University: Lviv, 2014.

Received: July 10, 2023 / Revised: August 16, 2023 / Accepted: September 01, 2023

ДОСЛІДЖЕННЯ ЗАКОНОМІРНОСТЕЙ НИЗЬКОТЕМПЕРАТУРНОГО ПІРОЛІЗУ ПОЛІЕТИЛЕНОВИХ ВІДХОДІВ

Анотація. *Одним із варіантів переробки відходів поліетилену є низькотемпературний піроліз, цільовим продуктом якого є піроконденсат. Вивчено фракційний склад і властивості піроконденсату піролізу поліетиленових відходів, одержаного за різних температур і тривалості. Проведено розділення піроконденсату на бензинову та дизельну фракцію і залишок. Встановлено склад і властивості цих фракцій та пов'язано їх з умовами процесу піролізу. Проведено рентгенофлуоресцентний аналіз піроконденсату і вузьких фракцій, виділених із нього.*

Ключові слова: *поліетиленові відходи, утилізація, піроліз, піроконденсат, рентгенофлуоресцентний аналіз, моторні палива.*