COMPREHENSIVE APPROACH TO POLYETHYLENE WASTE RECYCLING

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Abstract. Global chemical industry faced huge number of challenges last few years due to geopolitical situation. At the same time, ecological issues have become more critical and urgent. At the intersection of these challenges, we propose considering deep recycling of polyethylene waste, not only through incineration or production of secondary plastic. We aimed to investigate the possibility of obtaining fuel components from polyethylene waste using low-temperature pyrolysis up to 450 °C, followed by further product processing and chemical modification. We established their main tribological characteristics using standardized methods and performed gas chromatographic analysis. The gas phase primarily contains carbon mono- and dioxide, as well as propane (each about 20% (wt.)), ethane at 15% (wt.), methane at 5% (wt.), and traces of pentane and hexane. The process yields pyrolysis oil (more than 70% (wt.)) with unsaturated bonds as the main product. We carried out fractional distillation of the pyrolysis liquid into fractions corresponding to the boiling points of gasoline and diesel. To improve the gasoline-boiling fraction, we performed homogeneous alkylation with pentane on an acid catalyst. To enhance the tribological characteristics of the diesel-boiling fraction, we conducted catalytic cracking on an aluminum-silicon catalyst. The resultant products do not contain unsaturated compounds. Thus, we demonstrated that low-temperature pyrolysis of polyethylene makes it possible to obtain motor fuel components while utilizing waste packaging containers.

Keywords: polyethylene, low-temperature pyrolysis, pyrolysis liquid, fuel, tribological characteristics.

Introduction

The global chemical industry has faced numerous challenges in recent years due to the evolving geopolitical landscape. The redistribution of oil, gas, and chemical flows forces all countries to constantly seek alternative sources of production. At the same time, environmental problems are becoming more critical and urgent. According to data [1], over the 30 years of Ukraine's independence, prior to the full-scale war, the population has decreased by about 20%, while the amount of municipal solid waste (MSW) has increased by more than 40%. In terms of its composition, MSW is not homogeneous. The share of polymer waste is 9-13% (wt.), pulp and paper waste – 10-15% (wt.), and food waste – 35-50% (wt.) [2]. It seems like a small amount. Unfortunately, 90% of MSW in Ukraine is still sent to landfills [2], where it is mostly buried. This approach to MSW management requires large areas of land (approximately 10,000 hectares) for disposal, making them unsuitable for use for an extended period and also causing pollution. In addition, due to military operations, the amount of land in Ukraine that requires reclamation has increased significantly [3], making the issue of MSW processing even more relevant. In addition to the danger to terrestrial and marine environments, polymer waste is also a source of global greenhouse gas emissions (slightly more than 3%). About 10% of them are formed during the destruction of polymers [4].

An analysis of the current state of scientific research indicates the intensive development of areas related to the chemical processing of polymer waste into valuable products (synthetic fuels, monomers and low-molecular organic compounds) [5-13]. Methods of processing plastic waste can be divided into mechanical (extrusion) and chemical (pyrolysis, hydrocracking and solvolysis) [7]. Pyrolysis is used for the disposal of difficult-to-recycle plastic packaging containers (for example, mixed or contaminated PE, PP and plastic mixtures). However, sorting of the starting material is critically important for its implementation. Previously, it was characterised by low selectivity due to the formation of carbon; however, the development of modern approaches has allowed the process to be directed towards conversion to liquid products with yields above 80% [8; 9]. A universal and reliable method for obtaining liquid fuel compositions from polyolefins is hydrocracking. However, it is suitable only for the above polymers, and also requires the use of a complex catalytic system and relatively harsh reaction conditions (for example, high-pressure hydrogen) [10; 11]. According to literature sources, solvolysis is best suited for recycling of PET and other polyesters, which makes it possible to obtain monomers with high selectivity. However, the biggest drawback of implementing this process is the use of solvents, which has a negative impact on the environment [12; 13]. Analysing all the above-described methods of recycling polymer packaging, taking into account their advantages and disadvantages, pyrolysis is currently the most effective. However, it also requires further development, since most often, developers

bypass the issue of recycling the gases formed, as well as handling the solid residue. Also, most researchers do not pay enough attention to improving the chemical characteristics of the resulting liquid "fuels", their fractionation, etc.

Materials and methods

High-density polyethene (HDPE) was chosen as the most common polyethene type used for packaging; also, this type allows for a higher quantity of pyrolysis oil compared to low-density polyethene (LDPE) [4]. To avoid unpredictable results from the experiment, we used primary HDPE to model the system, where the waste is 100% composed of the current polymer. Low-temperature pyrolysis (up to 450 °C) was also chosen due to its tendency to achieve more liquid products, which are much easier to purify and modify. A laboratory installation for HDPE pyrolysis was created. It allows for all products collection: gases, pyrolysis oil, and solid residual (waxes). During pyrolysis, a slight heating flow rate was chosen, which also allows maximising the liquid products yield. Additionally, this installation was utilised for separating pyrolysis oil into two fractions: a light fraction boiling up to 180 °C (Fraction 1) and a heavy fraction boiling in the range of 180-300 °C (Fraction 2). To improve the tribological characteristics of Fraction 1, alkylation was performed, and Fraction 2 was obtained through catalytic cracking on the K-38 aluminium-silicon catalyst, as previously described [14].

The study examined the autooxidation kinetics of the obtained liquid with the antioxidant 2,6-di-*tert*-butyl-4-methylphenol (Ionol). The analysis was performed on a gasometric installation, using the volumetric method in kinetic mode (Fig. 1). Under kinetic oxidation conditions, the installation measures oxygen absorption rates from 10^{-8} to 10^{-4} mol·(l·s)$^{-1}$ at a substrate conversion of 0.1-1.0%. The random measurement error is 3-6% [15].

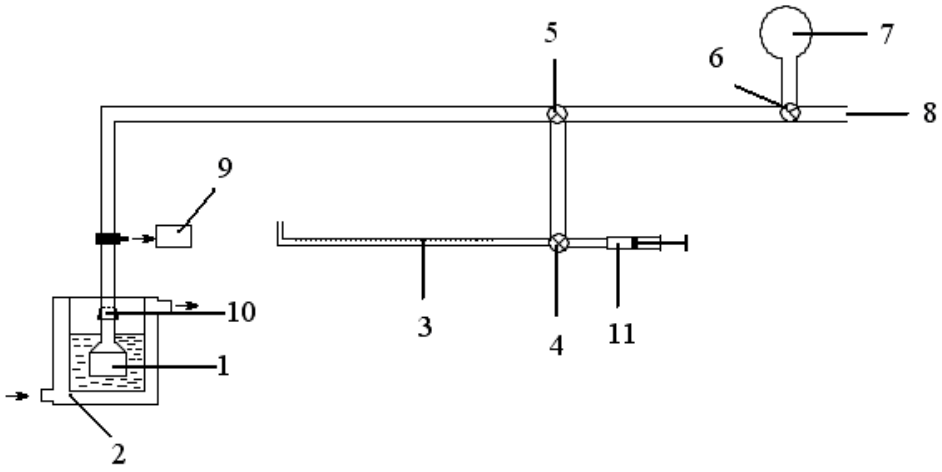

Fig. 1. **Gasometric unit for oxidation of organic compounds**: 1 – reactor; 2 – beaker for temperature control; 3 – gas burette; 4-6 – taps; 7 – oxygen chamber; 8 – ground joint for connection to a vacuum pump and purging the system with air; 9 – device for mixing the reaction mass; 10 – ground joint for connecting to the reactor

The qualitative and quantitative composition of gaseous and liquid products was determined using gas chromatography. Analysis of inorganic gases (H_2, CO, CO_2) and methane was carried out using a Chrom-5 gas chromatograph (Czech Republic) equipped with a thermal conductivity detector (TCD). Analysis of organic reaction products was performed using an Agilent Technologies 7890A gas chromatograph (USA) equipped with a flame ionization detector (FID). Data processing was performed based on chromatographic peak areas using the internal normalization method with calibration coefficients.

The following chemmotology studies were performed: saturated vapour pressure (DSTU EN 13016-1, DSTU 4160), fractional composition (EN ISO 3405, ASTM D86), study of anti-wear properties of fuel and lubricants (ASTM D2783, ASTM D2596), and determination of research octane number.

Results and discussion

It has been established that during HDPE pyrolysis, solid (wax), liquid (oil), and gas are formed. Table 1 shows the average weight yields in% of products after HDPE low-temperature pyrolysis. The composition of the gas fraction obtained during the above-described process was analysed by gas chromatography. It has been established that the main components are CO, CO_2, propane (each about 20% (wt.)), ethane at the level of 15% (wt.), methane – 5% (wt.), traces of pentane and hexane. After gas separation, hydrocarbons can be used either for further chemical processes or as a high-energy gas. Carbon oxides are a valuable raw material for obtaining methanol using the method we have improved [16]. The composition of gases under our conditions differs significantly from the data given in [17; 18], where carbon oxides are completely absent. The main gas there is propene (more than 40% (wt.)). This difference may be due to the conditions of GC analysis. Organic and inorganic components are identified by different detectors (flame ionisation and thermal conductivity, respectively), as noted in the previous section.

Table 1

Distribution of HDPE pyrolysis products: yield, mass %

Gas	Liquid	Solid residue	Losses
8.03	78.39	12.58	1.00

Solid residue (waxes) has shown the density 0.79 $g \cdot cm^{-3}$ and softening temperature range 42-44 °C and can be used like a component for technical greases and lubricants or like a high calorie energy source. Also it can be purified by the activated carbon for other purposes.

The main product is a liquid saturated and unsaturated hydrocarbons mix (C_5-C_{28}), which corresponds to works [18-22]. Fractional distillation of the pyrolysis liquid obtained in the process of HDPE low-temperature pyrolysis into fractions was carried out (Fig. 2) similar to work [22].

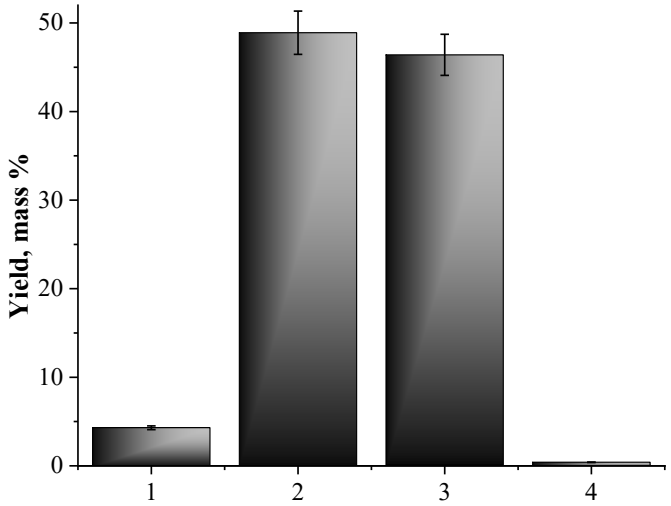

Fig. 2 **Fractional distillation of HDPE pyrolysis liquid:**
1 – gas; 2 – Fractions 1; 3 – Fractions 2; 4 –residue

Fraction 1 showed quite a low octane number – 50 and saturated vapour pressure of 3.4 kPa. Gas chromatographic analysis shows that more than 60% by weight of Fractions 1 and 2 consist of monoolefins. For enhancing the tribological and operational properties of Fraction 1, it is possible to increase the number of isomeric compounds in it due to the alkylation process. According to literature data, it is optimal for starting materials with a sufficient number of unsaturated compounds [23]. After alkylation, a fraction was obtained that boils under the conditions of a gasoline fraction and has an octane number of about 70, which is typical for straight-run gasoline. Its saturated vapour pressure was determined. It is 16.82 kPa. According to gas chromatographic analysis, unsaturated olefins are absent in the obtained alkylate. This approach to improving the chemical characteristics of the liquid fraction from low-temperature pyrolysis of HDPE has been used for the first time. Currently, all research on polymer recycling focuses only on thermolysis methods and the physicochemical characterisation of the

products formed [18-22]. However, there are no works on their further improvement and bringing the characteristics to marketable products.

The tribological characteristics of Fraction 2 were tested on a four-piece rubbing machine. It has been established that they are characterised by the indicator $Pk = 274$ N versus $Pk = 314$-360 N, characteristic of a commercial diesel engine. The fragments, as previously stated, are more than half carbohydrate-rich and non-saturated, so the burning material is not stable. Therefore, an antioxidant additive (Ionol) was added to our attention. The value increases to $Pk = 314$ N, which indicates the lower limit of anti-seize for a commercial product. Previously, such studies of the liquid fraction from low-temperature pyrolysis of HDPE were not conducted.

The volume of acid was measured volumetrically at a temperature of 75 ± 0.2 °C (Fig. 3), which was absorbed by the reaction system (Fraction 2) in time. This approach to assessing the chemical characteristics of the studied liquids was used for the first time, although it is generally accepted for classical fuels and lubricants [24]. The fluidity of the oxidation Fraction 2 (W) was determined by the tangents of the cut-off of the kinetic curve of the clayey acid. Antioxidative activity was assessed at the stage of reduction in cob liquidity of clay acid with oxidised Fraction 2, without (*1*) and in the presence of the antioxidative additive Ionol at a concentration of 0.05% (*2*).

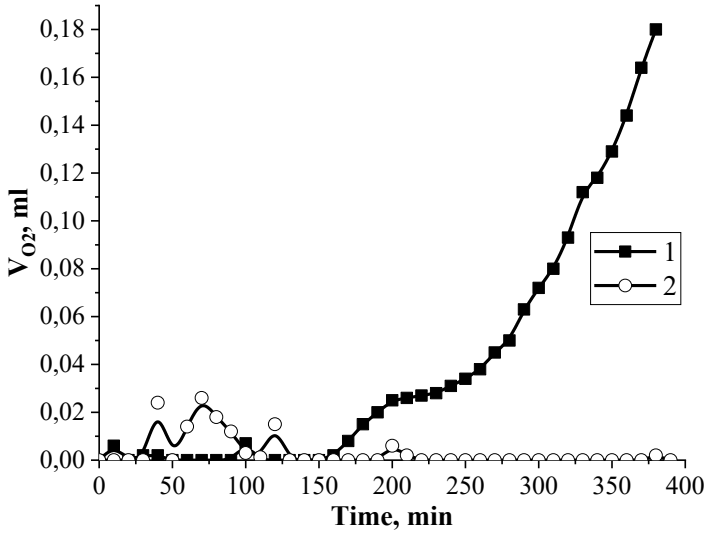

Fig. 3. **Kinetics of atmospheric oxygen absorption by Fraction 2 in the absence of inhibitor (1) and in the presence of Ionol (2)**

In the absence of an inhibitor (Ionol), the oxidation process by Fraction 2 proceeds as follows:

- 2.5 hours (initial period of the process), we observe inhibition of the oxidation process by Fraction 2 (induction period);
- then the oxidation process by Fraction 2 enters the auto-acceleration mode (after 2.5 hours from the start of oxidation – $W = 7.45\ 10^{-8}$ mol·(l·s)$^{-1}$; 3-4 hours – $W = 1.12\ 10^{-7}$ mol·(l·s)$^{-1}$; 5-6.5 hours – $W = 2.95\ 10^{-7}$ mol·(l·s)$^{-1}$.

The Ionol's introduction at a concentration of 0.05% into the oxidised Fraction 2 initially leads to a decrease in the oxidation rate (W) and subsequently to a complete inhibition of the oxidation process (Fig. 3, *1*). Ionol causes intensive inhibition of the chain-radical oxidation of Fraction 2 without any reaction mixture colour changes throughout the experiment. Therefore, initial studies of the features of the uninhibited and Ionol-inhibited autoxidation of Fraction 2 were conducted for a total time period of approximately 6.5 hours.

To improve the tribological characteristics of Fraction 2, its catalytic cracking was carried out. As a result, a liquid fraction was obtained that boiled under the conditions of commercial gasoline and had an octane number 78.2 (research method).

Conclusions

1. It is shown that during the pyrolysis of HDPE at 450 °C, the main product (more than 70% by weight) is a mixture of liquid unsaturated and saturated hydrocarbons. By gas chromatographic analysis, it was established that more than 60% by weight they consist of monoolefins. The determined physicochemical characteristics of the solid residue allow us to state the possibility of its use for technical greases and lubricants or like a high calory energy source.
2. Fractional distillation of the obtained liquid product was carried out into fractions that boil under gasoline (Fraction 1) and diesel (Fraction 2) conditions. Chemmological methods of research established that due to the high content of unsaturated compounds, they have unsatisfactory characteristics. To eliminate them, it is necessary to either introduce antioxidant additives or improve their characteristics through petrochemical processes.
3. It is shown that the introduction of the antioxidant additive Ionol allows not only to improve the extreme pressure characteristics of Fraction 2 but also to inhibit oxidation processes in it.
4. It has been established that the Fraction 1 alkylation reaction can produce a product with an octane number 20 points higher and a vapour pressure almost five times higher. Catalytic cracking of Fraction 2 allows for the production of a product that boiled off under the conditions of a gasoline fraction with an octane number of about 78.

Acknowledgements

We thank the Armed Forces of Ukraine for safety to carry out this work. This work was only possible thanks to the resilience and courage of the Ukrainian Army. Our priceless thanks to the heroic soldiers of the Ukraine Army, who protect us from Russian aggressors at the cost of their lives.

Author contributions

Conceptualization, V.Y.; methodology, V.S. and B.K.; software, B.K.; validation, V.S. and B.K.; formal analysis, T.T and V.Y.; investigation, V.S., B.K. and V.Y; data curation, V.S., B.K., T.T. and V.Y; writing – original draft preparation, V.S.; writing – review and editing, T.T. and V.Y.; visualization, V.S. and B.K.; project administration, V.Y.. All authors have read and agreed to the published version of the manuscript.

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