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Technological Bases of Motor Gasoline Production from Secondary Polyolefin Raw Material

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Abstract

The article proposes expanding the raw material base for the production of automotive gasoline by using secondary polyolefin raw materials (HDPE, PP). By processing the specified raw materials by pyrolysis in reactor-type devices at atmospheric or elevated pressure, it is possible to partially satisfy the need for a shortage of automotive gasoline. The influence of the technological parameters of pyrolysis (temperature (t, °C), pressure (P, MPa) and process duration (τ, min.)) on the volumetric yield of pyrolysis gases and gasoline fraction p.c.-180°C was investigated. It was found that with an increase in these parameters in the studied intervals (t=380-450°C, P=0.1-2.0 MPa and τ=30-90 min.) there is a significant (from 6 wt. % to 18 wt. %) increase in the yield of the fraction b.p.-180°C. In order to create rational compositions of commercial automobile gasolines, the need to compound the obtained fraction b.p.-180°C with volatile hydrocarbon fractions obtained from oil or gas condensate raw materials has been substantiated.

Keywords: *Gasoline, Polyolefins; Processing; Pyrolysis; Technological parameters; Reactor; Fractionation; Volatile hydrocarbons; Compounding.*

1. Introduction

In recent years, Ukraine has been experiencing an acute shortage of motor fuel such as motor gasoline. The rapid growth of Ukraine's car fleet, a significant shortage of high-quality hydrocarbon feedstock for the production of motor gasoline, and the destruction of oil refineries as a result of military operations can be attributed to the main reasons that contributed to this. Under the current conditions, Ukraine must import significant quantities (over 1 million tons/year) of automotive gasoline from such European Union (EU) countries as Sweden, Poland, Lithuania, Greece, etc. Thus, the issue of the development of the domestic oil refining industry is becoming quite acute today. Work related to the use of alternative raw materials and the development (improvement) of technologies for the production of automotive gasoline from these raw materials will reduce Ukraine's dependence on partner countries in meeting its own needs in automotive gasoline.

2. The objective of the research

The main direction in expanding the raw material base of the automotive gasoline production process is the use of secondary raw materials, in particular polymeric ones. Due to its processability and chemical composition similar to oil fractions, this raw material can be successfully processed into components (base fractions) of motor gasoline. Significant advantages of such raw materials are their low cost, significant volumes (both accumulated raw materials and those generated annually), and the need for their recycling due to the waste management directives adopted in the EU [1-4]. It should be noted that the initial polymer raw materials, such as polyethylene (LDPE, HDPE) and polypropylene (PP), do not contain resinous and asphalt substances and olefins, do not contain tar and asphalt substances and olefins, which significantly complicate refining processes and degrade the quality of the final product - motor gasoline. However, the specified polyolefins may contain up to 0.5-1 wt. % additives (antioxidants, fillers, dyes, etc.), which worsen their properties as raw materials for the production of motor gasoline. The main part of the metals and heteroatoms contained in the polymer raw materials during its processing remains in the high-boiling fractions and solid residue. However, in some cases, to increase the purity of the product, the obtained gasoline fractions can be additionally subjected to filtration, adsorption.

The content of sulfur-containing compounds in this feedstock ranges from 100-300 ppm, which also makes this feedstock quite attractive for the production of motor gasoline, which, according to [5], has rather stringent requirements – the content of sulfur-containing compounds in gasoline that meets the Euro-5 standard should not exceed 10 ppm. Thus, recycled polymer feedstocks can solve the problem of the shortage of classical (oil or gas condensate) hydrocarbon feedstocks in the production of motor gasoline. The implementation of such technology at existing enterprises has significant prospects, as it will partially resolve acute environmental issues that hinder integration processes between Ukraine and the EU.

The main process, which is quite successfully used in the global oil refining industry, aimed at obtaining from high-molecular hydrocarbon raw materials products of lower molecular weight, which correspond to the gasoline fraction, is pyrolysis [6-8]. This process does not require significant production costs for its implementation and can be implemented in mobile installations or at so-called "mini" oil refineries [9-10]. This is quite relevant, as it allows processing plants to be located near places where secondary raw materials are generated or accumulated. The mobility of enterprises is especially relevant in the context of hostilities.

It should be noted that the technological parameters that significantly affect the yield of gasoline fractions during the pyrolysis of polymer raw materials are the temperature (t, °C), pressure (P, MPa) and time (τ, min) of pyrolysis [11-13]. It is the yield of gasoline fraction as the target product of production that characterizes the economic feasibility of production as a whole [14]. Therefore, our study will be devoted to the study of the change in this indicator depending on the variation of the above-mentioned pyrolysis parameters.

3. Materials and methods of the research

Materials. The main materials of the study are high-density polyethylene (HDPE) with a density of 948 kg/m^3 and polypropylene (PP) with a density of 910 kg/m^3. These types of polyolefins are among the most common materials used for the production of household and industrial products of various functional purposes [15].

Methods. The production of gasoline fractions from the specified polymer raw materials was carried out according to the scheme presented in Fig. 1.

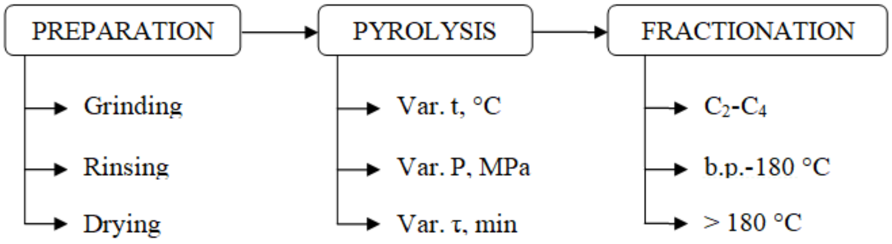

Figure 1. Structural scheme for obtaining gasoline fractions from polymer raw materials.

According to the presented scheme, in laboratory conditions, using a reactor-type apparatus similar to that used in works [16-18], pyrolysis of the selected polyolefin raw material was carried out at the following technological parameters: t= 380-450°C; P= 0.1-2.0 MPa; τ=30-

90 min. Then the obtained products were separated into a gas fraction (C_2-C_4); a gasoline fraction (b.p.-180°C); a residual fraction (>180°C).

The methods used in the study of pyrolysis products were standard and were presented in ASTM D5002-19 and ASTM D86.

4. Results and discussion

The results of experimental studies for HDPE and PP are presented in Fig. 2-9, respectively.

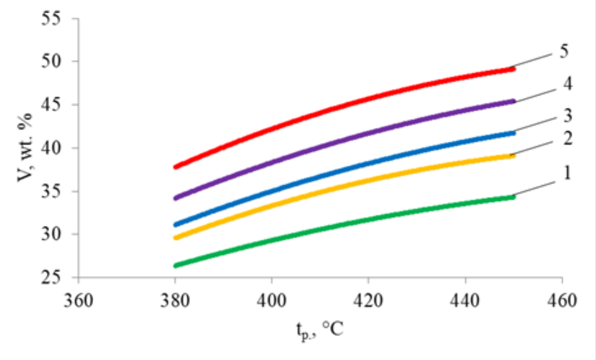

Figure 2. Dependence of V on $t_{p.}$ for the fraction b.p.-180°C (HDPE): 1–P=0.1 MPa; 2–P=0.5 MPa; 3–P=1.0 MPa; 4–P=1.5 MPa; 5–P=2.0 MPa.

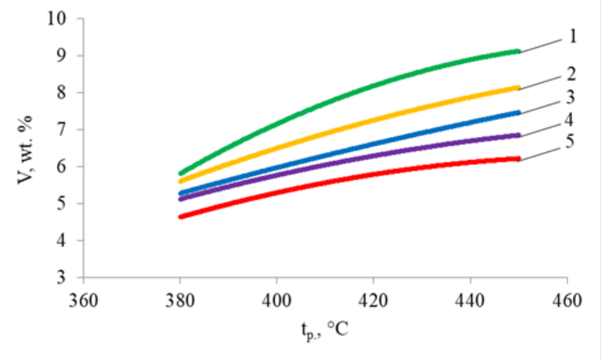

Figure 3. Dependence of V on $t_{p.}$ for gas (HDPE): 1–P=0.1 MPa; 2–P=0.5 MPa;3–P=1.0 MPa; 4–P=1.5 MPa; 5–P=2.0 MPa.

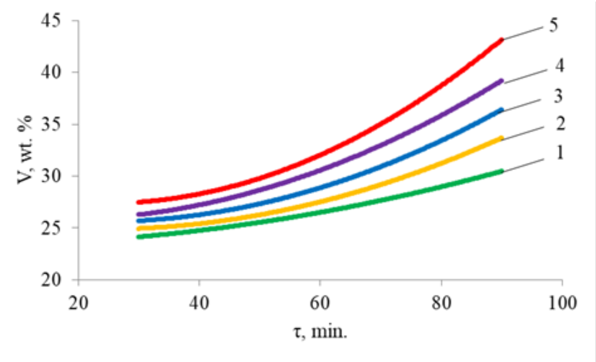

Figure 4. Dependence of V on τ for the fraction b.p.-180°C (HDPE): 1–P=0.1 MPa; 2–P=0.5 MPa; 3–P=1.0 MPa; 4–P=1.5 MPa; 5–P=2.0 MPa.

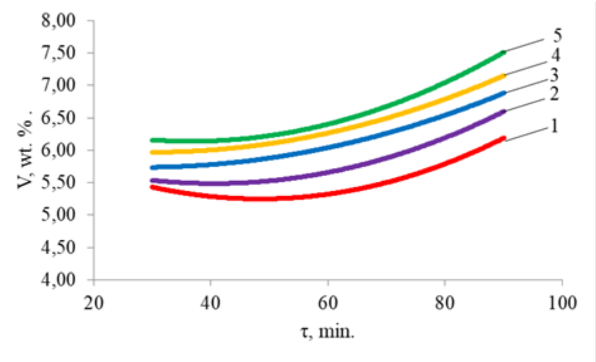

Figure 5. Dependence of V on τ for gas (HDPE): 1–P=0.1 MPa; 2–P=0.5 MPa;3–P=1.0 MPa; 4–P=1.5 MPa; 5–P=2.0 MPa.

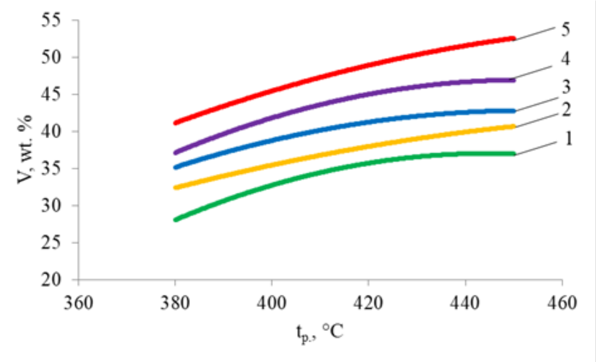

Figure 6. Dependence of V on $t_{p.}$ for the fraction b.p.-180°C (PP): 1–P=0.1 MPa; 2–P=0.5 MPa; 3–=1.0 MPa; 4–P=1.5 MPa; 5–P=2.0 MPa.

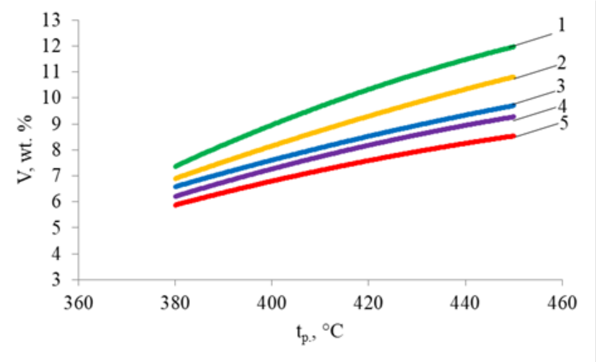

Figure 7. Dependence of V on $t_{p.}$ for gas (PP): 1–P=0.1 MPa; 2–P=0.5 MPa; 3–P=1.0 MPa; 4–P=1.5 MPa; 5–P=2.0 MPa.

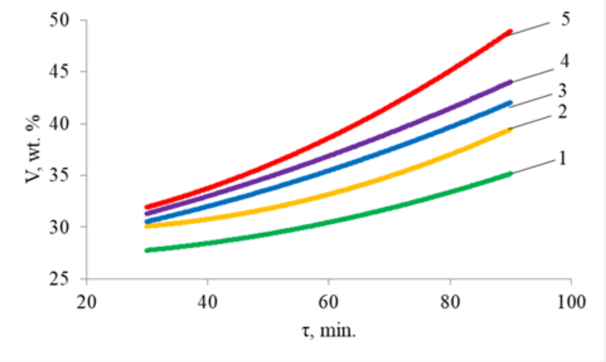

Figure 8. Dependence of V on τ for the fraction b.p.-180°C (PP): 1–P=0.1 MPa; 2–P=0.5 MPa; 3–P=1.0 MPa; 4–P=1.5 MPa; 5–P=2.0 MPa.

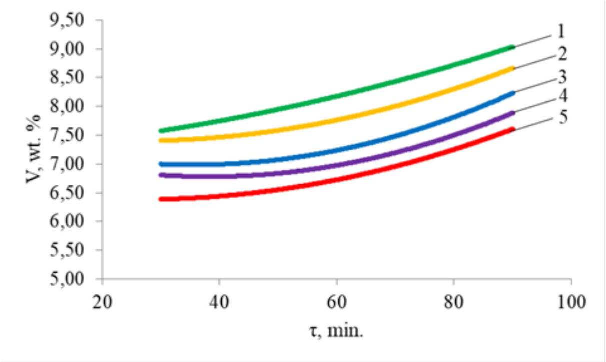

Figure 9. Dependence of V on τ for gas (PP): 1–P=0.1 MPa; 2–P=0.5 MPa; 3–P=1.0 MPa; 4–P=1.5 MPa; 5–P=2.0 MPa.

The obtained dependences indicate an increase in the yield of the b.p.-180°C fraction with an increase in temperature, pressure, and pyrolysis time, regardless of the type of polymeric raw material. With an increase in the pyrolysis temperature from 380°C to 450°C, depending on the pressure, for HDPE this increase is 8.1-11.28 wt. %; for PP, the increase is 8.72-13.13 wt. %. With an increase in pressure from 0.1 MPa to 2.0 MPa, the yield of fractions b.p.-180°C increases depending on the temperature. Thus, for HDPE, the increase is 11.80-14.88 % mass; for PP, the increase is 13.87-16.28 wt. %. Increasing the residence time of polymeric raw materials in the reaction zone contributes to the formation of a larger amount of the fraction b.p.-180°C due to intensive decomposition reactions of the hydrocarbon backbone of polymers. Thus, when the pyrolysis time is changed from 30 min to 90 min, at t = 400°C and pressure P=0.1-2.0 MPa, this increase is in the range: for HDPE – 6.58-16.24 wt. %.

As for the hydrocarbon gases of pyrolysis (C_2-C_4), changes in temperature, pressure and pyrolysis time affect the amount of their formation in a similar way as in the case of the gasoline fraction b.p.-180°C. Increasing the temperature and time of pyrolysis contributes to the formation of more gases, which is a negative phenomenon in the production of gasoline fraction. However, by increasing the process pressure from 0.1 MPa to 2.0 MPa, there is a significant reduction (for HDPE by 0.7-2.9 wt. %; for PP by 1.15-3.43 wt. %) of pyrolysis gases, but the process of gasoline fraction production is somewhat complicated.

Analyzing the obtained dependences, it should also be noted that due to the chemical structure of PP (every second atom of the hydrocarbon chain is tertiary), all C-C bonds in the hydrocarbon chain are less thermally stable than HDPE [19]. Therefore, under the same pyrolysis conditions, a slightly larger amount of both pyrolysis gases and a gasoline fraction b.p.-180 °C is formed from PP. The identical nature of the obtained dependences can be explained by the similarity of the structure of the selected polymers, which both belong to the class of polyolefins [20].

The dependences of physicochemical parameters (fraction boiling point ($t_{b.p.}$, °C); fraction density at 15°C (ρ^{15}, kg/m^3) and the amount of volatile fractions boiling up to 70°C (V^{70}, % vol.) of the fraction b.p.-180°C on pressure (P, MPa), at t = 400°C and τ = 30 min, are shown in Figs. 10-12.

According to the results obtained, it is obvious that the pressure at which the pyrolysis of the starting polyolefin feedstock occurs also significantly affects such indicators as $t_{b.p.}$, ρ^{15}, and V^{70}. With an increase in pressure from 0.1 MPa to 2.0 MPa, the $t_{b.p.}$ decreases by 22°C for HDPE and by 24°C for PP. The boiling point of a fraction is very important in the production of motor gasoline. It characterizes gasoline storage conditions, starting properties, and the ability to form vapor plugs in the internal combustion engine power system. $t_{b.p.}$ values of 62-67°C are not acceptable for commercial motor gasoline, as they should be within 30-40 °C. Such gasoline, due to the absence of volatile fractions that boil up to 60°C, is easier to store but has unsatisfactory starting properties. Carrying out the pyrolysis process under a pressure of 2.0 MPa, it is possible to obtain gasoline fractions with a $t_{b.p.}$ of 38-45°C. When producing commercial motor gasoline, such fractions need to be blended with volatile hydrocarbon fractions (e.g., isobutane, isopentane).

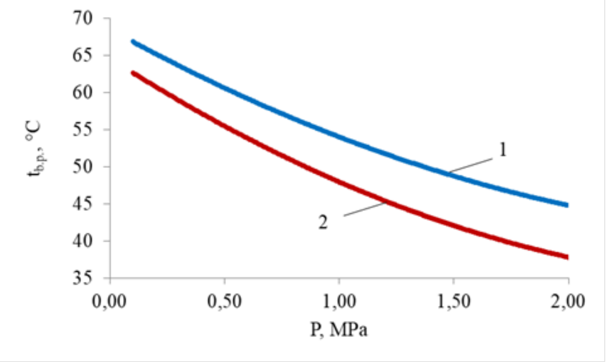

Figure 10. Dependence of $t_{b.p.}$ on P for the fraction b.p.-180°C: 1 – HDPE; 2 – PP.

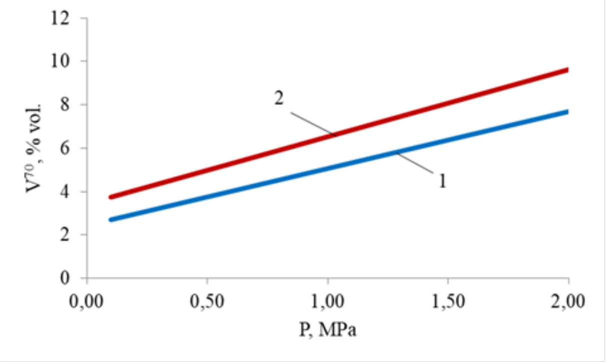

Figure 11. Dependence of V^{70} on P for the fraction b.p.-180°C:1 – HDPE; 2 – PP.

The motor gasoline V^{70} indicator, like the $t_{b.p.}$ indicator, is responsible for the starting properties. By increasing the pyrolysis pressure from 0.1 MPa to 2.0 MPa, the content of volatile fractions that boil off by 70 °C increases: for HDPE by 5.3 % vol. and for PP by 5.7 % vol.

According to [5], this indicator should be in the range of 20-50 % vol. For the fractions obtained by us, this indicator was in the range of 7.3-9.7 % vol., which indicates unsatisfactory starting properties and the need to compound them with hydrocarbon fractions that boil up to 70°C.

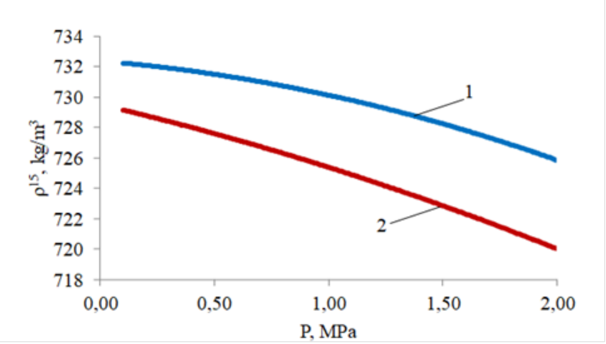

Figure 12. Dependence of ρ^{15} on P for the fraction p.k.-180 °C: 1 – HDPE; 2 – PP.

Such an important physicochemical indicator of motor gasoline quality as ρ^{15} also depends significantly on the pyrolysis pressure. Density is often used in technical, economic and transportation calculations. Increasing the pyrolysis pressure from 0.1 MPa to 2.0 MPa causes a decrease in ρ^{15} of the fraction b.p.-180°C. Thus, for HDPE, this decrease is 6 kg/m^3; for PP, it is 9 kg/m^3. Note that the reduction of ρ^{15} of motor gasoline provides some depletion of the fuel-air mixture, so the specific gasoline consumption decreases [21]. The values of ρ^{15} of the obtained samples of the fractions b.p.-180°C were in the following limits: for HDPE - 726-732 kg/m^3; for PP - 720-729 kg/m^3, which meets the requirements (720-755 kg/m^3) according to [5].

5. Conclusions

The possibility of partially compensating for the need for commercial motor gasoline by involving secondary polyolefin raw materials represented by high-density polyethylene (HDPE) and polypropylene (PP) in the production process is substantiated. The article analyzes the positive aspects (reserves, manufacturability, low sulfur content, absence of tar and asphalt substances) of the raw materials that will allow their use in the production of commercial gasoline through the pyrolysis process in mobile installations and "mini" refineries.

The influence of technological parameters (temperature, pressure, and duration) of the pyrolysis process of polyolefin feedstock on the amount of the formed gasoline fraction, which boils within the range b.p.-180°C, was analyzed. It was found that with an increase in the pyrolysis temperature from 380°C to 450°C, the yield of the indicated fraction increases by 8.1-11.28 wt. % (for HDPE) and by 8.72-13.13 wt. % (for PP). Increasing the pressure from 0.1 MPa to 2.0 MPa increases the fraction yield by 11.80-14.88 wt. % (for HDPE) and by

13.87-16.28 wt. % (for PP). Increasing the pyrolysis time from 30 minutes to 90 minutes increases the gasoline fraction yield by 6.58-16.24 wt. % (for HDPE) and by 7.85-17.6 wt. % (for PP).

Increasing the pressure at constant temperatures and duration of pyrolysis of polymeric raw materials also helps to reduce the boiling point of the gasoline fraction (by 22°C for HDPE and 24°C for PP); increases the content of volatile fractions that boil up to 70°C (by 5.3 % vol. for HDPE and 5.7 % vol. for PP); and reduces the density (by 6 kg/m^3 for HDPE and 9 kg/m^3 for PP).

The results obtained indicate the possibility of using the fraction b.p. -180°C as a basic component of commercial automobile gasoline together with volatile hydrocarbon fractions obtained from classical oil or gas condensate raw materials.

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