Original article

UDC 665.752

DOI: 10.15372/CSD2025657

EDN: OOYWTL

Study of the physicochemical characteristics of thermolysis oil from polypropylene

V. S. KRESTYANINOVA[1,2] ✉, A. V. SAIKO[1,2], P. A. DOLGUSHEV[1], O. V. KLIMOV[1]

[1]*Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia*

[2]*Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia*

E-mail: kvs@catalysis.ru✉, saiko@catalysis.ru, dolgushevpa@catalysis.ru, klm@catalysis.ru

Abstract

Physicochemical characteristics of thermolysis oil obtained from polypropylene have been determined. The hydrocarbon composition, studied by two-dimensional gas chromatography and high performance liquid chromatography, as well as calculation of the iodine value, shows that the major components of the resulting oil are isoalkanes and alkenes. The results obtained allow us to draw conclusions about the mechanism of polypropylene transformation during thermolysis, and data on the fractional composition, density and viscosity further characterise thermolysis oil from the perspective of a petroleum product.

Keywords: polypropylene, thermolysis oil, thermolysis, plastic waste, macromolecule decomposition mechanism, oil refining, diesel fuel

Funding: the work supported by the Russian Science Foundation (Project No. 22 13-20013) and the Novosibirsk Region (Agreement No. r-5 of 06.04.2022).

For citation: Krestyaninova V. S., Saiko A. V., Dolgushev P. A., Klimov O. V., Study of the physicochemical characteristics of thermolysis oil from polypropylene, *Chemistry for Sustainable Development*, 2025, Vol. 33, No. 3, P. 297–302. DOI: 10.15372/CSD2025657. EDN: OOYWTL.

INTRODUCTION

The problem of plastic waste utilisation is extremely urgent and holds global importance because the world production of plastics demonstrates a stable growth trend. At present, about 400 mln t of various kinds of plastics are manufactured in the world, and according to predictions, by 2050 about 12 000 mln t of accumulated plastic wastes will be disposed to waste landfills or into the environment [1].

Plastics are used is daily life as packaging material [2], clothes and sports equipment [3], biomedical devices [4], electronic components [5], and in many other areas. Most plastics are obtained from non-renewable oil reserves. The urgent need of the access to new technologies for plastics processing and repeated use is evident, keeping in mind the origin of plastic materials and their harmful effects on the environment [6, 7]. One of the most promising methods to process plastic wastes is considered to be thermolysis.

Thermolysis is an endothermic non-catalytic process, which is carried out at a high temperature, within the range of 500–800 °C as a rule, resulting in the formation of volatile mixture, which is later on separated into the condensable liquid fraction and non-condensable hydrocarbon

gases, solid coke or other solid residues [8]. The composition of products obtained by thermolysis depends on the properties of raw materials, process temperature, pressure, residence time and heating rate [9, 10]. The main product of the thermolysis of the plastic wastes is thermolysis oil (TO).

Polypropylene (PP) is still one of the most extensively used polymer materials because of its chemical stability, low density, and high melting point in comparison with other similar polymers, which allows using PP to fabricate thermally resistant products [11]. Polyolefins account for about 66.9 % of all plastics in solid residential wastes [12], and they do not contain heteroatoms, which defines their potential suitability for processing to obtain valuable hydrocarbon products. Publications often provide descriptions of thermolysis, either for PP alone [13, 14] or in mixture with other plastics [15–17], however, the possibility to introduce the resulting products into oil refining processes has not been studied previously.

In the previous works, we have studied the physicochemical properties of mixed TO from real domestic wastes [18], and demonstrated that it can be used as an alternative to modern petroleum products and involved in such processes as hydroprocessing and catalytic cracking [19]. However, due to the heterogeneity of domestic waste composition, first, it is impossible to obtain TO with the same characteristics all the time, and second, the physicochemical properties of TO cannot be predicted. For this reason, a detailed investigation of the transformations of individual polymers during thermolysis appears to be a relevant task along the route of plastic waste processing and introducing the products into classical oil refining processes.

The goal of the present work was to determine the physicochemical characteristics of thermolysis oil obtained from polypropylene, and to assess the possibility to introduce this product into oil refining processes as alternative raw material, or as an additive to traditional petroleum products.

EXPERIMENTAL

Preparation of thermolysis oil from polypropylene

Thermolysis oil was obtained using a set-up of periodic action. Polypropylene (Stavrolen LC, Russia) was loaded into a quartz reactor 2 L in volume and heated from the room temperature to 430 °C at a rate of 8 °C/min in nitrogen flow. Nitrogen was supplied into the reactor at a flow rate of 30 mL/min. The liquid product obtained during heating was kept at 430 °C for 1 h. The yield of thermolysis oil was 53 wt%.

Determination of the content of aromatic compounds in thermolysis oil

Determination of the content of aromatic compounds in TO was carried out according to ASTM D6591 procedure by means of high-performance liquid chromatography (HPLC) using an Agilent 1260 Infinity chromatograph (Agilent Technologies, USA) equipped with the system of silica gel – amine columns. Analysis results are characterised by precision <5 rel%.

Determination of the group composition of thermolysis oil by two-dimensional gas chromatography

Determination of the group composition of TO was carried out by two-dimensional gas chromatography (GC-GC) using an Agilent GC 7890B gas chromatograph (Agilent Technologies, USA) equipped with a CFT modulator, automatic liquid sampler Agilent 7693A and a flame ionisation detector (FID) (380 °C, 50 Hz). Analysis conditions: non-polar first-measurement column VF-5ht UltiMetal, medium-polarity second-measurement column DB-17HT (50 % phenyl)-methylsiloxane (Agilent Technologies, USA).

Determination of the fractional composition of thermolysis oil

The distribution of TO boiling ranges was determined using ASTM D7213 procedure. The studies were carried out with an Agilent 7890B gas chromatograph with the flame ionisation detector by means of simulated distillation. The samples were preliminarily diluted with carbon disulphide to decrease viscosity. Analysis results are characterised by the error of 2–5 °C.

Determination of the density and viscosity of thermolysis oil

Dynamic, kinematic (calculated) viscosity and density were determined according to ASTM D7042 procedure using Stabinger viscosity and density meter SVM 3000 (Anton Paar, Austria). Viscosity and density were measured at a temperature of 40 °C. The precision of analysis results is 5 rel%.

Determination of the elemental composition of thermolysis oil

Elemental analysis was performed with an automatic CHNS-analyser EURO EA 3000 (Eurovector Instruments, Italy). Sampled were weighted with a Sartorius CP2P balance (Germany). Sample combustion proceeded in a vertical reactor in the dynamic mode at 1050 °C in He flow with the addition of O_2 (10 mL) at the moment of sample introduction. The formed gases, namely N_2, CO_2, H_2O and SO_2, were separated on a column with PoraPak Q adsorbent and determined using a thermal conductivity detector (katharometer). Calculation was carried out with Callidus software supplied with the analyser.

Iodine value

Determination of the iodine value per 100 g of the product and recalculation for the mass fraction of unsaturated compounds were carried out according to GOST 2070-82. This standard regulates the method to determine iodine values and the mass fractions of unsaturated hydrocarbons in gasoline, propellants, diesel fuel, and other light oil products. A weighted portion of thermolysis oil was dissolved in acetone, iodine solution in ethanol was added, and the mixture was kept for 5 min. The sample solution was titrated with a 0.1 M solution of sodium thiosulphate using an automatic potentiometric titration apparatus Akvilon ATP-02 (Russia) equipped with platinum and silver chloride electrodes, up to a jump in potential. The equivalence point was determined with the device software Titrate 5.0 Base within the accuracy of 0.01 mL.

RESULTS AND DISCUSSION

The main goal of the work was to determine the physicochemical parameters of TO obtained from polypropylene, to confirm the mechanism of its transformation during thermolysis, and to study the possibility of introducing it as an alternative raw material into the fuel processes of classical oil refining. The choice of analysis procedures is due to their applicability to TO analysis and the possibility to obtain the results allowing TO characterisation considering it as a petroleum product [20]. The fractional composition of TO from PP is shown in Fig. 1. It may be stressed that the percentage of light fractions (gasoline and diesel) was 40 and 34 %, respectively. This

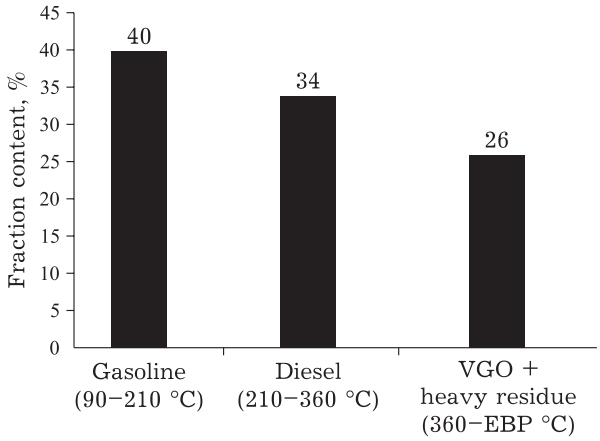

Fig. 1. Fractional composition of thermolysis oil from polypropylene, determined by simulated distillation. VGO – vacuum gas oil, EBP – the end boiling point.

allows assuming that the major components of TO are C_6–C_{34} hydrocarbons. The results of determination of the density, kinematic viscosity, elemental composition, the content of aromatic compounds and unsaturated hydrocarbons are presented in Table 1. The C/H ratio, calculated from the elemental composition, confirms this result. Kinematic viscosity of TO from PP (1.9 mm^2/s) at 40 °C corresponds to the viscosity of diesel fuel (2.0–4.5 mm^2/s). The density of TO at 40 °C is within the range characteristic of the gasoline and diesel fractions (0.69–0.84 g/cm^3). Thus, relying on the physicochemical characteristics of TO, we may decide whether the obtained product can be used as an alternative to the gasoline and diesel fraction of oil.

To carry out detailed investigation of the hydrocarbon composition and to obtain reliable results, TO from PP was analysed using three different methods: HPLC – to determine the content of aromatic compounds, GC-GC – to study

TABLE 1

Main characteristics of thermolysis oil from polypropylene

Parameter	Value
Kinematic viscosity, mm^2/s (at 40 °C)	1.9
Density, g/cm^3 (at 40 °C)	0.77
Content, wt%:	
carbon	86.0
hydrogen	14.0
monoaromatic hydrocarbons	0.8
diaromatic hydrocarbons	0.1
polyaromatic hydrocarbons (three and more cycles)	0.1
unsaturated hydrocarbons	14.0

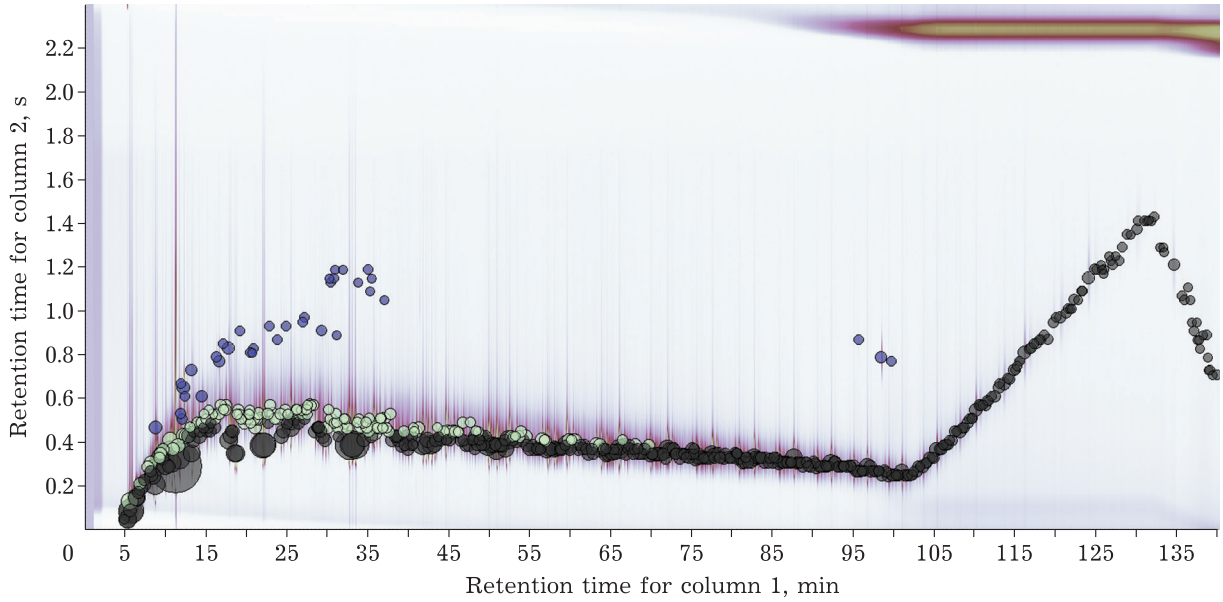

Fig. 2. Chromatogram of thermolysis oil from polypropylene, recorded by high-temperature two-dimensional gas chromatography.

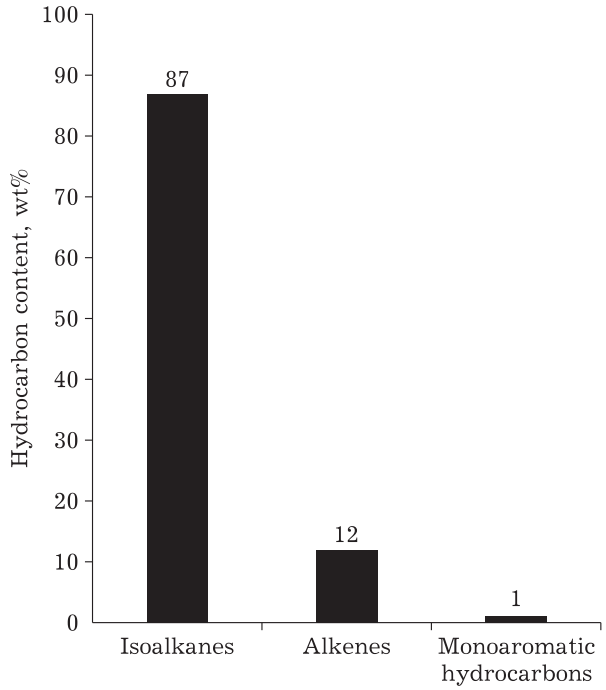

Fig. 3. Hydrocarbon composition of thermolysis oil from polypropylene, determined by high-temperature two-dimensional gas chromatography.

the group composition, determination of iodine value – to reveal the content of unsaturated hydrocarbons. One can see (Table 1) that the total percentage of aromatic compounds is 1.0 wt%. This is evidence that the main products of thermal decomposition of polypropylene are aliphatic hydrocarbons. By recalculating the iodine value for TO from PP, the content of unsaturated hydrocarbons was determined to be 14 wt%.

The hydrocarbon composition of TO from PP was studied in detail by high-temperature two-dimensional gas chromatography. The chromatogram is presented in Fig. 2. The hydrocarbon composition of TO is shown in Fig. 3. One can see that the major hydrocarbons in TO are isoalkanes and alkenes, while the content of monoaromatic compounds was 1.0 wt%. This agrees with the result obtained by HPLC (0.8 wt%). The content of alkenes determined by GC-GC was 12 wt%. This result agrees with the content of unsaturated hydrocarbons determined by the measurement of iodine value (14 wt%). The agreement between the results obtained using different methods allows assessing the reliability of experimental data and correctness of the choice of procedures for the analysis of TO from PP.

The procedure used to determine the hydrocarbon composition allows demonstrating the distribution of hydrocarbons over oil fractions (Table 2). Results of the investigation of the total content of components in fractions, obtained by GC-GC and simulated distillation (see Fig. 1), agree with each other, which also confirms their reliability.

Judging from the data on hydrocarbon composition obtained by GC-GC, HPLC according to ASTM D6591 procedure, as well as according to State Standard GOST 2070-82, it may be concluded that the main classes of hydrocarbons in

TABLE 2

Distribution of hydrocarbons over petroleum fractions in thermolysis oil, wt%

Hydrocarbon composition	Fraction			
	Gasoline ($<C_{12}$)	Diesel (C_{12}–C_{20})	Vacuum gas oil (C_{21}–C_{37})	Heavy residue ($>C_{37}$)
Isoalkanes	35.9	26.5	20.6	4.0
Alkenes	4.7	6.2	1.1	<0.01
Monoaromatic hydrocarbons	0.8	0.1	0.1	<0.01
Total	41.4	32.8	21.8	4.0

TO are isoalkanes and alkenes. This fact agrees with the literature data on polypropylene transformation during pyrolysis. Indeed, it is known that thermal degradation of polypropylene leads to hydrocarbon chain cleavage (mainly between secondary and ternary carbon atoms), which results in the presence of mainly isoparaffins and olefins in the final products [21]. The products exhibit broad molecular mass distribution. The yield of gas is usually low, so the liquid fraction is the major product of thermolysis [22, 23]. Thus, the literature data are confirmed by the results obtained by the analysis of TO from PP (see Tables 1, 2 and Fig. 2, 3).

We have demonstrated that a highly aliphatic product is formed during polypropylene thermolysis at 430 °C. This can be considered as a valuable characteristic of the TO because makes it possible to use TO as an alternative raw material or an additive to straight-run diesel fuel, because aliphatic compounds are ignited at low temperature and pressure and are useful fuel components.

On the basis of the data on the fractional composition, density, viscosity and C/H ratio, it may be concluded that thermolysis oil from PP is suitable for introducing into the fuel processes of classical oil refinement. This opens broad possibilities for processing the plastic wastes. It should be mentioned that the percentage of PP in plastic wastes is 26 %. Therefore, the hydrocarbon composition of thermolysis oil from PP will have a positive effect on the quality of TO from a mixture of different plastics enriching it with aliphatic branched isoalkane molecules.

CONCLUSION

The physicochemical characteristics of thermolysis oil obtained from polypropylene, namely fractional composition, density, viscosity, elemental and hydrocarbon composition, the content of aromatic compounds and unsaturated hydrocarbons, were studied using different methods. It is shown that the major products of polypropylene thermolysis in the absence of air at 430 °C are isoalkanes and alkenes. This fact is experimental confirmation that the destruction of a macromolecule proceeds through the cleavage of bonds between the secondary and tertiary carbon atoms. It is shown that TO from PP is comparable in kinetic viscosity and density with such oil products as straight-run diesel fuel and straight-run gasoline fraction. For oil refinement and waste utilisation purposes, the fractions of TO from PP obtained by fractional distillation can be used as additives to the above-listed petroleum products.

REFERENCES

1. Kovaleva N. Yu., Raevskaya E. G., Roshchin A. V., Plastic waste pyrolysis – a review, *Chemical Safety Science*, 2020, Vol. 4, No. 1, P. 48–79. (In Russ.).
2. Malik N., Kumar P., Shrivastava S., Ghosh S. B., An overview on PET waste recycling for application in packaging, *Int. J. Plast. Technol.*, 2017, Vol. 21, No. 1, P. 1–24.
3. Kaufmann J., New materials for sports equipment made of anisotropic fiber-reinforced plastics with stiffness related coupling effect, *Procedia Eng.*, 2015, Vol. 112, P. 140–145.
4. McKeen L. W., Plastics used in medical devices, in: Handbook of Polymer Applications in Medicine and Medical Devices, K. Modjarrad, S. Ebnesajjad (Eds.), Elsevier, Amsterdam, 2014, P. 21–54.
5. Day M., Cooney J. D., Touchette-Barrette C., Sheehan S. E., Pyrolysis of mixed plastics used in the electronics industry, *J. Anal. Appl. Pyrolysis*, 1999, Vol. 52, No. 2, P. 199–224.
6. Hidalgo-Ruz V., Gutow L., Thompson R. C., Thiel M., Microplastics in the marine environment: a review of the methods used for identification and quantification, *Environ. Sci. Technol.*, 2012, Vol. 46, No. 6, P. 3060–3075.
7. Gestoso I., Cacabelos E., Ramalhosa P., Canning-Clode J., Plasticrusts: a new potential threat in the Anthropocene's rocky shores, *Sci. Total Environ.*, 2019, Vol. 687, P. 413–415.
8. López A., de Marco I., Caballero B. M., Laresgoiti M. F., Adrados A., Pyrolysis of municipal plastic wastes: influence of raw material composition, *Waste Manage.*, 2010, Vol. 30, No. 4, P. 620–627.
9. López A., de Marco I., Caballero B. M., Laresgoiti M. F., Adrados A., Torres A., Pyrolysis of municipal plastic waste II: influence of raw material composition under catalytic conditions, *Waste Manage.*, 2011, Vol. 31, No. 9–10, P. 1973–1983.

10. Chin B. L. F., Yusup S., Al Shoaibi A., Kannan P., Srinivasakannan C., Sulaiman S. A., Kinetic studies of co-pyrolysis of rubber seed shell with high density polyethylene, *Energy Convers. Manage.*, 2014, Vol. 87, P. 746–753.
11. Polypropylene Handbook: Polymerization, Characterization, Properties, Processing, Applications, E. P. Moore (Ed.), Hanser Publishers, Munich, 1996, 419 p.
12. Buekens A. G., Schoeters J. G., Technical methods in plastics pyrolysis, *Macromol. Symp.*, 1998, Vol. 135, P. 63–81.
13. Abbas-Abadi M. S., Haghighi M. N., Yeganeh H., McDonald A. G., Evaluation of pyrolysis process parameters on polypropylene degradation products, *J. Anal. Appl. Pyrolysis*, 2014, Vol. 109, P. 272–277.
14. Jin Z., Chen D., Yin L., Hu Y., Zhu H., Hong L., Molten waste plastic pyrolysis in a vertical falling film reactor and the influence of temperature on the pyrolysis products, *Chin. J. Chem. Eng.*, 2018, Vol. 26, No. 2, P. 400–406.
15. Donaj P. J., Kaminsky W., Buzeto F., Yang W., Pyrolysis of polyolefins for increasing the yield of monomers' recovery, *Waste Manage.*, 2012, Vol. 32, No. 5, P. 840–846.
16. Klaimy S., Lamonier J.-F., Casetta M., Heymans S., Duquesne S., Recycling of plastic waste using flash pyrolysis – effect of mixture composition, *Polym. Degrad. Stab.*, 2021, Vol. 187, Art. 109540.
17. Singh R. K., Ruj B., Sadhukhan A. K., Gupta P., Thermal degradation of waste plastics under non-sweeping atmosphere: Part 1: Effect of temperature, product optimization, and degradation mechanism, *J. Environ. Manage.*, 2019, Vol. 239, P. 395–406.
18. Klimov O. V., Nadeina K. A., Saiko A. V., Krestyaninova V. S., Vatutina Yu. V., Bogomolova T. S., Salomatina A. A., Dolgushev P. A., Studying properties of hydroconversion products of thermolysis oil produced from waste of mixed plastics, *Ekologia i Promyshlennost Rossii = Ecology and Industry of Russia*, 2023, Vol. 27, No. 2, P. 15–21. (In Russ.).
19. Klimov O. V., Nadeina K. A., Potapenko O. V., Vatutina Yu. V., Saiko A. V., Koveza V. A., Mukhacheva P. P., Krestyaninova V. S., Yurtaeva A. S., Bogomolova T. S., Salomatina A. A., Gerasimov E. Yu., Prosvirin I. P., Noskov A. S., Refining of chlorine-containing plastic wastes by traditional hydrotreating and catalytic cracking processes, *Fuel*, 2023, Vol. 349, Art. 128651.
20. Krest'ianinova V. S., Saiko A. V., Dolgushev P. A., Pchelnikova T. G., Nadeina K. A., Klimov O. V., A set of methods for studying thermolysis oils and products of their hydrogenation processing, *J. Sib. Fed. Univ. Chem.*, 2023, Vol. 16, No. 1, P. 87–95. (In Russ.).
21. Wampler T. P., Thermometric behavior of polyolefins, *J. Anal. Appl. Pyrolysis*, 1989, Vol. 15, P. 187–195.
22. Kaminsky W., Zorriqueta I.-J. N., Catalytical and thermal pyrolysis of polyolefins, *J. Anal. Appl. Pyrolysis*, 2007, Vol. 79, No. 1–2, P. 368–374.
23. Predel M., Kaminsky W., Pyrolysis of mixed polyolefins in a fluidised-bed reactor and on a pyro-GC/MS to yield aliphatic waxes, *Polym. Degrad. Stab.*, 2000, Vol. 70, No. 3, P. 373–385.

Submitted 05.07.2024
Approved 21.08.2024
Accepted 25.09.2024