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Light Hydrocarbon Liquids Production by Co-Pyrolysis of Polypropylene and Hydrolytic Lignin

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Abstract

The effect of components ratio in the mixture composed of atactic polypropylene and hydrolytic lignin on the yield of products and composition of the light (b.p. < 180 °C) hydrocarbon fraction formed during the pyrolysis of the mixture under autoclave conditions in inert atmosphere at 400 °C is investigated. It is established that the addition of lignin in the amount of 20 to 40 % of the mixture mass provides a substantial increase in the yield of light hydrocarbons. The liquid products with the maximum yield of the light fraction (52 % mass) were obtained with the 30 % mass of lignin in the initial mixture. Analysis of the composition of light hydrocarbon products by means of ATR spectroscopy and GC-MS showed that these products are mainly formed as a result of thermal decomposition of polypropylene. The specific contribution from lignin in the co-pyrolysis with polypropylene is expressed as an increase in the content of C_9 hydrocarbons and β-olefins in the light fraction.

INTRODUCTION

More than 120 mln t of synthetic polymers had been synthesized at the end of the XX century in the world. A trend to permanent growth of their production is observed [1]. The amount of waste formed during production and use of the polymers is correspondingly increasing. For instance, in the countries of the European Community, in which different kinds of municipal domestic waste are collected separately, polymeric materials constitute more than 15 % of the waste [2].

In Russia, the amount of waste material formed in the production of polymers and products made of them, as well as in handling them, is also high [3, 4]. As a rule, recycling of the polymeric materials in the technological process is economically inefficient and difficult to be performed in many cases, therefore, a substantial part of such a waste is collected at disposal tips. It is known that polymeric materials decompose under natural conditions very slowly, which inevitably leads to the accumulation of their waste. These circumstances provide the necessity to develop ecologically safe methods of utilization of the polymeric waste and explain why the efforts of researchers in this area are increasing.

At present, the most widespread method of utilization of polymeric waste is combustion. However, this method is not only unsafe ecologically but also economically unreasonable because the composition of polymeric materials allows one to consider them as potential raw material for the production of valuable chemical products and components of motor fuel.

The simplest method of obtaining low-molecular compounds is based on thermal decomposition of polymeric materials. Pyrolysis of polyolefins in inert atmosphere or in vacuum at the temperature within the range 350–400 °C leads mainly to the formation of high-boiling hydrocarbons. The yield of light products increases with the pyrolysis temperature rise to 700 °C; however, a substantial amount of gaseous hydrocarbons and coke is also formed under these conditions [5].

The co-liquefaction of synthetic polymers with coal or biomass in inert gas or hydrogen has been investigated [6, 7]. Non-additive increase of conversion degree in polyethylene/coal mixtures was discovered, as well as an increase in the yield of liquid products from thermal decomposition in polyolefin/wood mixture. The observed phenomena were explained in terms of the interaction of radical fragments formed under thermal destruction of synthetic and natural polymers. It was discovered that the yield and composition of liquid hydrocarbon products are determined by the conditions under which the co-pyrolysis is conducted and by relative content of synthetic and natural polymers in the initial mixture [7–9]. Solid residues from the co-pyrolysis of the synthetic and natural polymers can be used as porous carbon materials. In particular, the possibility to obtain high-quality carbon sorbents by means of the co-pyrolysis of wood and polypropylene was demonstrated by the authors of [10, 11].

The hydrolytic lignin is a large-scale waste of wood processing; efficient methods of its industrial utilization are poorly developed yet. Interest to the development of new processes of co-transformations of lignin with synthetic polymers, in particular with polypropylene, aimed at obtaining carbon composite materials and chemical compounds has increased in the recent years [12–14].

In the present work, we investigate the effect of relative content of polypropylene and lignin in the initial mixture on the yield of products of their co-pyrolysis in inert atmosphere under the autoclave conditions and on the composition of the resulting light hydrocarbon fractions.

EXPERIMENTAL

Industrial samples of atactic polypropylene manufactured at the Tomsk Oil Chemical Plant (with particle size less than 1 mm) and hydrolytic lignin from the Krasnoyarsk Biochemical Plant (with particle size less than 0.1 mm) dried at 100 °C (1 % mass of moisture) were used in the investigation. Some characteristics of the initial materials are shown in Table 1.

The pyrolysis was performed in rotating autoclaves 0.25 l in volume at the temperature of 400 °C. A mixture of polypropylene with lignin (total mass being 12 g) was loaded into the autoclave. Content of the components in the initial mixture was varied from 0 to 100 % mass. Before experiments, the autoclave was blown with a ten-fold amount of argon to remove the air; the initial argon pressure was adjusted to be 0.3 MPa. Temperature in the autoclave was risen at the rate of 6 °C/min. The heated autoclave was kept at the necessary temperature for 1 h. The working pressure in the autoclave was 1.1–1.3 MPa. After soaking, the autoclave was cooled to the room temperature; the volume of gas-phase products was determined. The composition of gases was analyzed with LKhM 80 chromatograph

TABLE 1

Elemental composition of atactic polypropylene and lignin

Compound	Content, % mass				
	C	H	N	S	O*
Polypropylene	81.4	13.2	0	0	5.4
Lignin**	63.1	5.9	0	0.6	30.0

*Oxygen concentration is calculated using the difference: 100 − (C + H + N + S).

**Calculated per dry ash-free basis.

using the heat conductivity detector (katharometer) and columns with zeolite (to analyze CH_4 and CO) and PQ porapack (to analyze CO_2 and hydrocarbons). The low-boiling part of liquid products b.p.< 180 °C (light products) was collected directly from the autoclave by freezing them out into a trap cooled by liquid nitrogen at the pressure of 66.7 Pa; then these products were separated into the hydrocarbon and water fractions by decanting. The content of the autoclave was extracted with benzene. The extract was dried till constant weight under vacuum at the room temperature and at the pressure of 66.7 Pa. The yield of extract was determined by weighing. The resulting product was a mixture of liquid substances boiling above 180 °C (heavy products). The conversion degree of the organic mass of the mixture of lignin with the polymer was calculated taking into account the mass of solid residue insoluble in benzene.

The ATR spectra (Attenuated Total (Internal) Reflection) of the light fraction (with b.p. < 180 °C) were recorded with BIORAD FTS 185 instrument (MCT detector cooled with liquid nitrogen). The spectra were recorded within the range 4000–700 cm^{-1} with the resolution of 4 cm^{-1}. A standard Biorad Win-IR (3.01) software was used to process the spectra.

The content of individual hydrocarbons in the light fraction was determined by means of chromatomass spectrometry using the Agilent 6890 chromatograph equipped with the Agilent 5973 selective mass detector (70 eV). The products were separated with an Optima I No. 726839.50 (50 m × 0.2 m with OV-1) capillary column under the temperature programming from 40 to 185 °C at the rate of 3 °C/min. The compounds were identified using the NIST98 computer database.

RESULTS AND DISCUSSION

Effect of relative content of lignin and polypropylene in the initial mixture on the yield of products of their co-pyrolysis

The pyrolysis of polypropylene, lignin and their mixtures was performed at 400 °C in inert atmosphere. This temperature point was chosen on the basis of results of previous investigations which proved that the maximum yield of distillated products from the mixture of synthetic and natural polymers is achieved under these conditions.

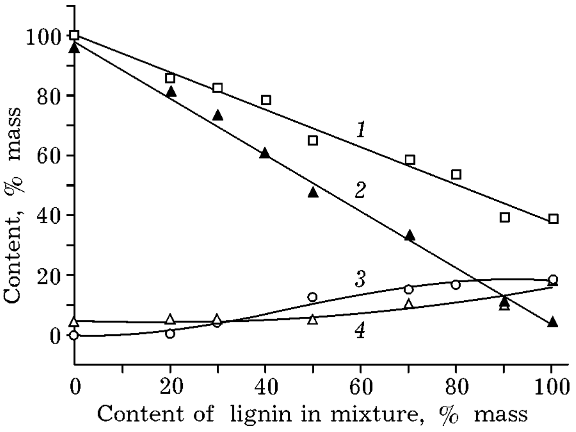

Fig. 1. Influence of hydrolytic lignin/polypropylene initial mixture composition on the parameters of the co-pyrolysis in inert atmosphere (400 °C, 1 h): *1* – degree of conversion, *2* – total yield of liquid products, *3* – yield of water fraction, *4* – yield of gases.

It follows from Fig. 1 that under these conditions polypropylene in the absence of lignin is almost completely converted into liquid and gaseous products, the yield of the former being predominant and equal to more than 95 % mass. The addition of hydrolytic lignin to polypropylene causes both a decrease in the conversion degree of the mixture and a decrease in the yield of liquid hydrocarbons; these parameters decrease proportionally to an increase in lignin content of the mixture. In the case of lignin pyrolysis in the absence of polypropylene, the conversion degree and the yield of liquid products are substantially lower than in the case of polypropylene pyrolysis (39 and 4 % mass, respectively). However, in the former case a high yield of gaseous products and water fraction containing water-soluble hydrocarbons is observed.

The relative content of light (<180 °C) and heavy (>180 °C) fractions in the liquid hydrocarbon products of the pyrolysis depends on the components ratio in the initial mixture (Fig. 2). In the case of the pyrolysis of polypropylene, mass fraction of heavy fraction in the liquid products is almost 80 %, which is in accordance with the known literature data [5].

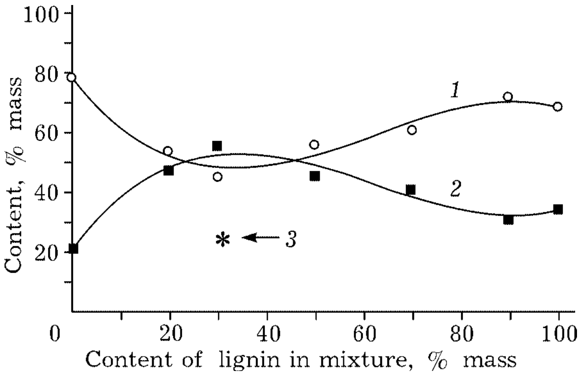

Fig. 2. Influence of content of hydrolytic lignin on the composition of hydrocarbon products of its co-pyrolysis with atactic polypropylene (400 °C, 1 h): *1* – fraction boiling above 180 °C; *2* – fraction with boiling point not higher than 180 °C; *3* – content of fraction with boiling point not higher than 180 °C, calculated from additive contribution from products of lignin and polypropylene pyrolysis with their mass ratio (%) 30 : 70.

Non-additive character of changes in the light to heavy fractions ratio in the liquid products depending on the lignin content of the lignin/polypropylene mixture was discovered. The addition of lignin in the amount of 20–50 % of the mass of initial mixture to polypropylene causes a substantial increase in the content of the light fraction boiling below 180 °C. Liquid products with maximum content of light fraction (52 % mass) were obtained after pyrolysis of the mixture containing 30 % mass of lignin and 70 % mass of polypropylene. This is 2.2 times as large as the sum of the yields of light fractions obtained independently during pyrolysis of lignin sample and polypropylene sample. Previously, we discovered a similar non-additivity phenomenon in the case of joint thermal transformation of beech wood and cellulose with polypropylene and polyethylene [9]. This phenomenon is likely to be due to chemical reactions between the reactive compounds formed under thermal decomposition of polypropylene and lignin.

It should be noted that the authors of [8, 15] did not discover non-additivity for the co-pyrolysis of wood biomass and polypropylene; the reason may be specific experimental procedure involved. Thermogravimetry allows one to record only total sample mass loss during thermal transformations but not the fractional composition of the formed products.

Composition of light hydrocarbon products of the co-pyrolysis of lignin and polypropylene

Figure 3 shows the ATR spectra of the light fraction formed under the pyrolysis of atactic polypropylene (curve *1*) and co-pyrolysis of polypropylene with lignin (curve *2*). Light products are represented mainly by paraffin and olefin hydrocarbons, which is evidenced by the presence of intensive absorption bands of aliphatic CH_2, CH_3 groups within the regions 2960–2870 and 1460–1380 cm^{-1}, as well as absorption bands at 1660 and 890 cm^{-1}, which can be assigned to the vibrations of C=C and C–H bonds, respectively, in the compounds of RR_1=C–H type. The comparison of the spectra shown in Fig. 3 suggests that the addition of lignin to polypropylene causes substantial changes in the composition of the liquid products of pyrolysis. This is observed in a decrease in the intensity of absorption bands at 890 and 1660 cm^{-1} and a decrease in the ratio of intensities of the absorption of CH_2 and CH_3 groups. Absence of intensive absorption bands in the regions characteristic of oxygen-containing groups indicates that the mixtures under analysis are mainly represented by the products of decomposition of the synthetic polymer: paraffins and olefins. Aromatic products of thermal conversion of lignin are present in this fraction only in insignificant amount.

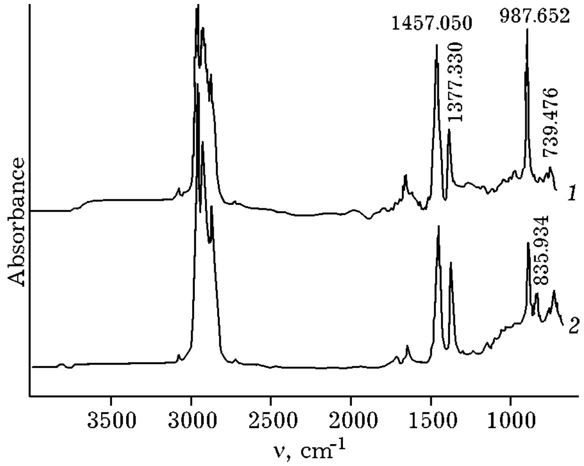

Fig. 3. ATR spectra of light fraction of liquid products of the pyrolysis of atactic polypropylene (*1*) and the joint pyrolysis of the mixture (mass ratio 1 : 1) of lignin and atactic polypropylene (*2*).

According to the data of chromatomass spectrometry, the light fraction formed in the pyrolysis of polypropylene contains about 200 individual compounds of different classes (paraffins, cycloalkanes, olefins and aromatic hydrocarbons); however, fractions of many compounds are insignificant in this fraction. The content of about 30 compounds is approximately 1 % and more. It follows from the data shown in Fig. 4, *b* that these hydrocarbons are mainly characterized by not very long retention time, *i. e.*, have relatively small molecular mass. The most substantial mass fraction is that of 2,4-dimethyl-1-heptene (up to 15.8 %). A characteristic feature of the polypropylene pyrolysis products is the presence of structural isomers of a-olefins in them.

Light fractions of the co-pyrolysis of polypropylene and lignin (see Fig. 4, *a*) have an increased content of the compounds with relatively large molecular mass, in comparison with polypropylene pyrolysis products. It was established that 2,4-dimethyl-1-heptene is predominant among individual hydrocarbons (its content is 14.7 % mass, which is 14.5 times as large as that in the products obtained by the pyrolysis of the polymer without lignin added). It is important to note that β-olefins

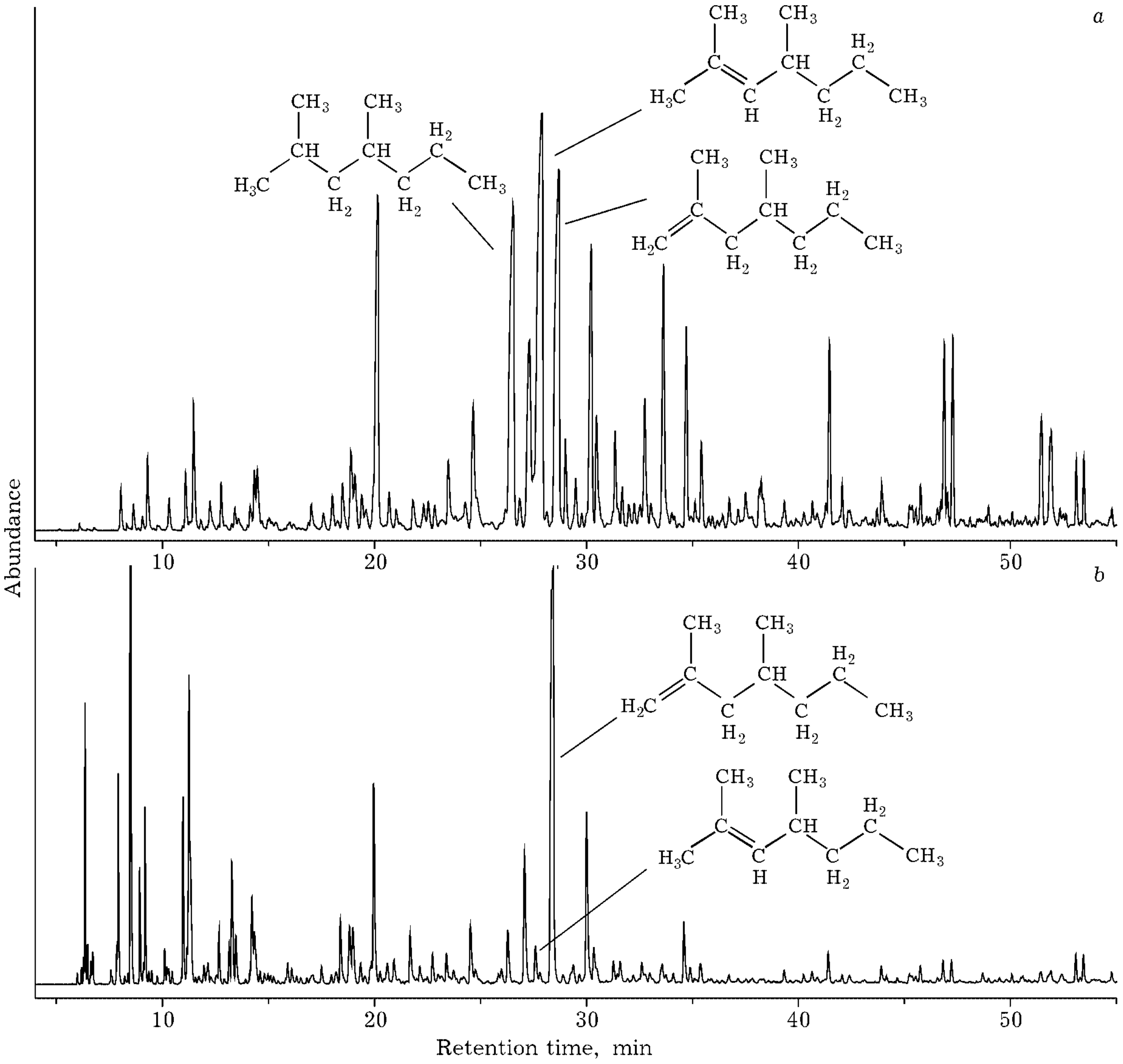

Fig. 4. GC-MS chromatograms of the light fraction (<180 °C) of the liquid products of the co-pyrolysis of lignin/atactic polypropylene mixture (mass ratio 1 : 1) (*a*), and pyrolysis of atactic polypropylene (*b*).

are prevailing in the light fraction of the co-pyrolysis of polypropylene and lignin. We observed such a change in the composition of light fraction previously in investigating the joint transformation of polypropylene with cellulose, as well as with beech and pine wood [9]; however, this change is much stronger expressed in the presence of lignin.

The character of the distribution of individual compounds in the light fractions of pyrolysis products over the classes and over the number of carbon atoms in molecule is shown in Figs. 5 and 6. It follows from the data obtained that the distribution of hydrocarbons over the indicated parameters is non-uniform for the products obtained both by the pyrolysis of polypropylene and by the co-pyrolysis of polypropylene with lignin. Three evident maxima are observed; they correspond to molecules with 6, 9 and 12 carbon atoms; a substantial part of these hydrocarbons is represented by olefins. However, there are some differences in the composition of light products obtained from polypropylene and from its mixture with lignin. For instance, the addition of lignin to polypropylene causes an increase in the content of hydrocarbons with 9 carbon atoms in molecule. Total mass fraction of these compounds in the light products of the co-pyrolysis of polypropylene and lignin is about 45 %, while their yield from polypropylene does not exceed 31 %. The addition of lignin to polypropylene also causes a decrease in the content of cyclic alkanes, which are represented mainly by trimethylcyclohexanes (see Figs. 5 and 6), and the concentration of aromatic hydrocarbons (Table 2). Aromatic hydrocarbons may be formed as a result of dehydrogenation of methylcyclohexanes followed by elimination of substituents, since partially dehydrogenated methylcyclohexane derivatives were detected in small amounts in polypropylene pyrolysis products.

It follows from the data presented in Table 2 that the presence of lignin causes an increase in the content of ethyl-, dimethyl- and trimethylbenzene in the light fraction of pyrolysis products, while benzene and methylbenzene content decreases.

Thus, analyzing the experimental data we may conclude that in the co-pyrolysis of poly-

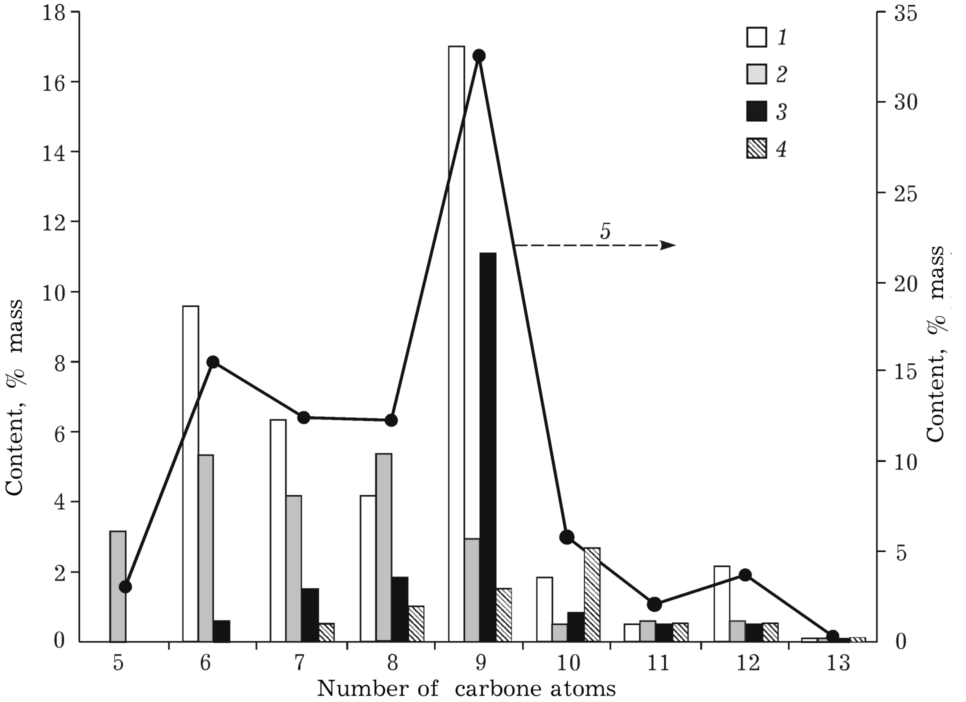

Fig. 5. Distribution of the individual hydrocarbons over classes and the number of carbon atoms in molecule for the light fraction (<180 °C) of liquid products of the pyrolysis of atactic polypropylene: *1* – olefins, *2* – paraffins, *3* – cycloalkanes, *4* – dienes, *5* – total hydrocarbon content.

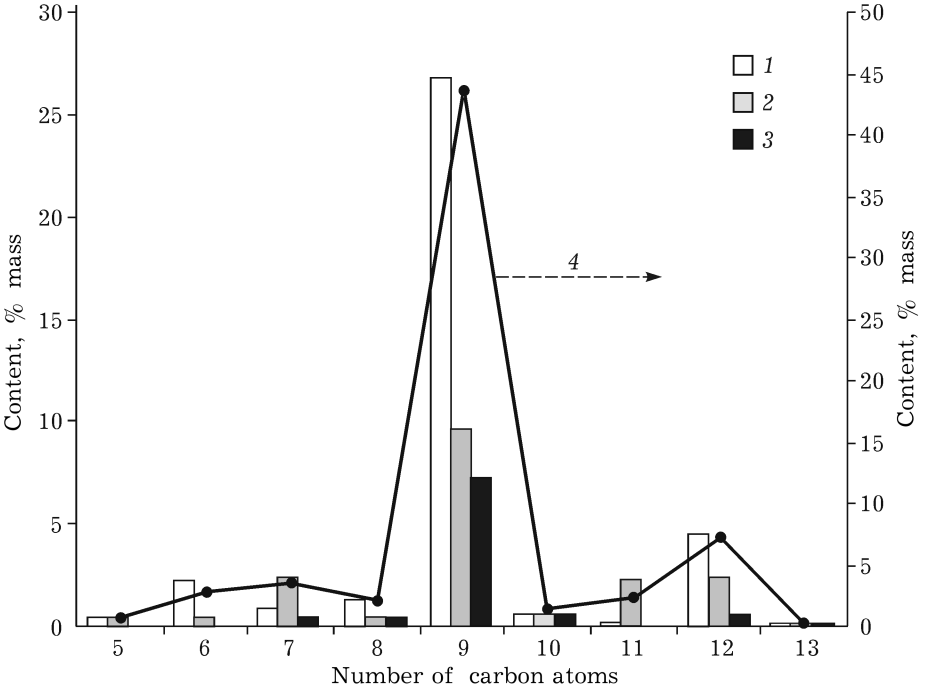

Fig. 6. Distribution of the individual hydrocarbons over classes and the number of carbon atoms in molecule for the light fraction (<180 °C) of liquid products of the pyrolysis of a mixture of lignin and atactic polypropylene (1 : 1): *1* – olefins, *2* – paraffins, *3* – cycloalkanes, *4* – total hydrocarbon content.

propylene and lignin in inert atmosphere light hydrocarbons are formed mainly as a result of thermal decomposition of polypropylene. Lignin has a substantial effect on thermal decomposition of polypropylene, which is exhibited by non-additive increase in the yield of light hydrocarbon products and in the changes in their chemical composition. For example, comparison of the data shown in Figs. 1 and 2 suggests that the yield of light fraction in the pyrolysis of polypropylene without lignin is 19 % mass. When the content of lignin added to polypropylene was 30 % mass, the content of distillate fractions was 55 % mass under the same pyrolysis conditions. This means that the yield of light products from polypropylene under the action of lignin additives has increased almost by a factor of 3. Thus, the addition of hydrolytic lignin to polypropylene under pyrolysis at not very high temperature (400 °C) provides high degree of the transformation of synthetic polymer into light liquid products and low extent of gas formation. The effect of lignin is also expressed in an increase in the content of C_9 hydrocarbons and β-olefins. Results of the investigation of composition of light liquid products show that they can be considered as raw material for producing valuable chemical compounds and motor fuel components.

Technological schemes of the utilization of synthetic polymers by means of pyrolysis in inert atmosphere, mastered abroad using in-

ТАБЛИЦА 2

Effect of composition of the raw material under pyrolysis on the content of aromatic hydrocarbons in the light hydrocarbon fraction of pyrolysis products

Compound	Content in pyrolysis products, % mass	
	polypropylene	polypropylene/lignin mixture (1 : 1)
Benzene	7.53	0.20
Methylbenzene	1.83	1.38
Ethylbenzene	0.09	0.92
1,4-Dimethylbenzene	1.74	1.97
1,3-Dimethylbenzene	0.21	0.54
1,2,3-Trimethylbenzene	1.50	3.18
Total	13.90	8.19

stallations with the productivity up to 200 t/day include two main stages: pyrolysis of polymers at 390–410 °C, and hydrogenation of the light constituent of the pyrolysis products under mild conditions resulting in gasoline species, which are most valuable products. Gaseous products are utilized by combustion; the heavy part of pyrolysis products is used as additives in manufacturing plastics [16, 17]. Lignin addition at the first stage of those processes would allow one to increase the yield of light fraction sharply.

High olefin content of the heavy liquid products of the co-pyrolysis of lignin and polypropylene allows considering them as a promising raw material for the production of surfactants like alkyl sulphates and alkene sulphonates [18].

CONCLUSIONS

In the pyrolysis of polypropylene at 400 °C, the addition of hydrolytic lignin causes an increase in the yield of hydrocarbon fraction with boiling point not higher than 180 °C. With 30 % lignin content (calculated per the mass of the mixture), the yield of light products from polypropylene increases almost by a factor of 3 and reaches content of 55 % mass.

Light hydrocarbon products of the co-pyrolysis of polypropylene and lignin are formed mainly as a result of thermal decomposition of polypropylene. Specific contribution from lignin is an increase in C_9 hydrocarbons and β-olefins content in the light fraction.

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REFERENCES

1 J. P. Hannequart, C. Allen, B. Dewulf, Proc. of Premier forum européen sur les déchets, Bruxelles, 16–17 nov., 1997, p. 1–20.

2 G. E. Zaykov, *Sorosovskiy obrazov. zhurn.,* 12 (2000) 48.

3 Munitsipal'nye i promyshlennye otkhody: sposoby obezvozhivaniya i vtorichnoy pererabotki. Ekologiya: Analit. obzory, izd. NGU, Novosibirsk, 1995, issue 39.

4 Gos. dokl. “O sostoyanii okruzhayushchey prirodnoy sredy v Rossiyskoy Federatsii v 1991 g.”, *Zeleny mir,* 1992, No. 39–44.

5 S. L. Madorsky, Thermal Degradation of Organic Polymers, Interscience publ., 1967.

6 V. I. Sharypov, B. N. Kuznetsov, A. V. Golovin *et al., Khimiya v interesakh ustoychivogo razvitiya,* 5 (1997) 201.

7 F. P. Gulyurtlu, M. Gongalves, I. Cabrita, Proc. 8th Europ. Conf. on Energy, Environment, Agriculture and Industry, Vienna, 1994, p. 318.

8 E. Jakab, G. Varhegyi, O. Faix, *J. Anal. Appl. Pyrolysis*, 59 (2000) 273.

9 N. G. Beregovtsova, V. I. Sharypov, B. N. Kuznetsov *et al.*, Book of Proc. IV Intern. Symp. “Catalytic and Thermochemical Conversion of Natural Organic Polymers”, May 30 – June 3, 2000, Krasnoyarsk, 2000, p. 67.

10 J. Simitzis, J. Sfyrakis, *J. Anal. Appl. Pyrolysis*, 26 (1993) 37.

11 G. Collot, Y. Zhuo, D. R. Dugwell, R. Kandiyoti, *Fuel*, 78 (1999) 667.

12 S. Kubo, J. F. Kadla, R. Venditti, R. D. Gilbert, 11th ISWPC Intern. Symp. on Wood and Pulping Chemistry, Nice, France, June 11–14, 2001, pp. 47–50.

13 R. A. Young, G. Toriz, F. Denes, *Ibid.,* pp. 79–82.

14 C. Pouteau, B. Monties, B. Cathala *et al.*, *Ibid.,* pp. 59–62.

15 Y. Matsuzawa, M. Ayabe, J. Nishino, *Polymer Degradation and Stability*, 71 (2001) 435.

16 *Petrole inf.*, 1708 (1995) 58.

17 V. Francois, *Usine nouv*, 2475 (1994) 53.

18 N. N. Lebedev, Khimiya i teknologiya organicheskogo i neftekhimicheskogo sinteza, Khimiya, Moscow, 1988.