Thermal Processing of Hydrolytic Lignine in Petroleum Residue

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Abstract

Process of joint thermal processing hydrolytic lignine and black oil fuel within the temperature range of 350–415 °C at atmospheric pressure has been investigated. The basic products of the process are represented by liquid distillate products evolved out of the reactor, and a cracked residue within the reactor. The addition of lignine accelerates to a considerable extent the reactions of liquid-phase thermal cracking of the petroleum residue and causes the yield of distillate products to increase. Basing on the obtained data concerning the composition of the products of joint thermal processing of lignine and petroleum residue the ways of their practical use are offered.

Key words: lignine, petroleum residue, joint pyrolysis, distillate products, thermal cracked residue

INTRODUCTION

The pyrolysis of the vegetative biomass as a renewed raw resource is extensively studied with the purpose of obtaining liquid fuel products, biofuel [1–3], as well as chemical raw [4]. One of the main components of the biomass is presented by lignine that is contained in plants to the extent from 15 to 36 % and exhibits macromolecular structure [5].

Hydrolytic lignine represents a waste product resulting from chemical processing of wood. The pyrolysis of lignine as one of possible lines of its recycling [6] is actively studied with the purpose of obtaining liquid organic products [1, 4] and carbon sorbents [7–9].

Carrying out the pyrolysis of organic compounds of macromolecular nature in solvents allows one to improve the conditions of heat and mass transfer processes and to lower the process temperature. Moreover, a solvent could take part in the process pyrolysis thereby influencing the composition of the products un-

der formation. With the joint pyrolysis of the biomass and the petroleum residue used as a solvent, the obtaining biofuels is made possible whose composition include both organic products of thermal decomposition of the biomass with considerable oxygen content [2], and the products of hydrocarbon nature formed in the reactions of the liquid-phase cracking of petroleum residue [10]. The joint pyrolysis of the petroleum residue and waste products of sugar-cane in vacuum was investigated by the authors of [11] who have revealed a synergetic effect presented by an increase in the yield of carbon residue under the pyrolysis of the mixture. The laws of joint pyrolysis of the petroleum residue and the biomass (rubber-bearing plant Calotropis procera) at 460 °C were considered in [12], and the products of this process have been studied by the authors of [13].

This work is devoted to the presentation of the results of studying the process of joint thermal processing of hydrolytic lignine and petroleum residue.

EXPERIMENTAL

In this work we used lignine with moisture content amounting to 3.0 mass % and with the following chemical composition, %: C 59.5, H 6.4, N 0.2, (S + O) 33.9, H/C = 1.29 Petroleum residues such as tar and bitumen were applied as solvents. Tar exhibited the following characteristics: the density of 1012 kg/m^3; the softening temperature value (according to a Ring and Ball method) being of 34 °C; the asphaltene content amounting to 16.7 %; the elemental composition, %: C 85.5, H 11.2, N 0.5, (S + O) 2.8, H/C = 1.57. The elemental composition of bitumen, %: C 85.7, H 10.7, N 0.3, (S + O) 3.3, H/C = 1.50.

The thermal processing of petroleum residue, lignine and their mixtures was carried out at atmospheric pressure in a metallic reactor of 150 ml in volume with a propeller agitator [14] within the temperature range of 350–415 °C. The vapour of condensing liquid products and gases were discharged through an outlet in a reactor dome. The duration of experiments ranged within 60–180 min after reaching a preset temperature. After completing an experiment the innage of the reactor (cracked residue) was unloaded in the liquid state; then it was subjected to the extraction with toluene using a Soxhlet extractor. Toluene insoluble substances were dried up to reaching constant weight at 105 °C, toluene soluble substances were isolated through toluene distillation under vacuum. The total amount of gases and losses were calculated basing on the difference between the mass of the reactor before the experiment and the sum of the values of the reactor mass after the experiment and the mass of distillate products.

The distillate products, toluene soluble and toluene insoluble substances were investigated using of the elemental analysis, Fourier transform IR spectroscopy and ^{1}H NMR spectrometry. IR spectra were obtained using a Perkin Elmer Spectrum BX-II Fourier Transform spectrometer. Liquid samples were suspended and tabletted with KBr, the IR spectra of toluene insoluble substances and lignine were registered in the solid using a diffuse reflection Fourier transform IR spectroscopy technique. ^{1}H NMR spectra of the distillate and toluene soluble

products were obtained with the help of a Bruker DRX-400 spectrometer with TMS as the internal standard in the CDCl$_3$ solution at a room temperature. The group composition of the fractions of distillate products was analyzed using a Shimadzu GC 17A gas chromatograph supplied with a flame ionization detector (GC-FID). All the data of the products investigation, unless the experiment duration otherwise specified, were obtained for the processing time amounting to 60 min.

RESULTS AND DISCUSSION

Yield of products

Liquid distillate products topped out of the reactor, non-condensing products (gas) and cracked residue in the reactor are formed under thermal processing of the individual petroleum residues and lignine within the temperature range under investigation from 350 to 415 °C. The distillate products of thermal cracking of the petroleum residue represent a light brown liquid with the density of 0.80–0.85 kg/dm^3 and exhibit a hydrocarbonic composition [15, 16]. The distillate products of lignine pyrolysis delaminate with the segregation of a top aqueous layer and a dark brown bottom layer of organic compounds with a high content of substituted phenols [6]. The distillate products of the joint process after the condensation spontaneously segregate resulting in the formation of the following three layers: a bottom layer of organic products and an itermediate aqueous layer, whose formation is connected with the thermal destruction of lignine, and a top layer of hydrocarbonic products resulted mainly from the thermal decomposition of tar.

The data on the product yields for the pyrolysis of tar, lignine and their mixtures are presented in Table 1.

Considerable deviations from the additivity are observed under thermal processing of the mixes of tar and lignine: the total yield of distillate products increases, the yield of gas and cracked residue in the reactor decreases. The apparent lignine conversion value calculated on assumption that the toluene insoluble fraction of cracked residue in the reactor consists only

TABLE 1

Thermal cracking of tar, lignine and their mixtures (the reaction time of 60 min)

Exp. No.	Reactor load, g		Temperature, °C	Mass of products, g				Lignine conversion level, %
	Tar	Lignine		Cracked residue	Toluene insoluble substances	Distillate products	Gas	
1	99.5	–	350	94.3 (94.8)	0	2.2 (2.2)	3.0 (3.4)	–
2	103.3	–	380	89.0 (86.2)	0	8.3 (8.0)	6.0 (5.8)	–
3	95.7	–	400	38.3 (40.0)	3.0 (3.1)	50.2 (52.4)	7.2 (7.5)	–
4	–	21.0	350	13.8 (65.7)	13.8 (65.7)	4.8 (22.9)	2.4 (11.4)	34.3
5	–	24.7	380	13.9 (56.4)	13.9 (56.4)	7.6 (30.8)	3.1 (12.7)	43.6
6	–	20.9	400	9.5 (45.5)	9.5 (45.5)	5.1 (24.4)	6.3 (30.1)	54.5
7	67	21.0	350	74.3 (84.4) 77.3 (87.8)	8.4 (9.5)	10.7 (12.2) 6.3 (7.2)	3.0 (3.4) 4.4 (5.0)	53.0
8	68	21.5	380	56.8 (63.2) 71.1 (79.1)	14.1	28.1 (31.3) 12.2 (13.6)	5.0 (5.5) 6.6 (7.3)	36.0
9	66	20.3	400	34.6 (40.0) 35.6 (41.3)	23.1	41.0 (48.0) 39.6 (45.9)	10.7 (12.0) – (12.8)	–

Notes. 1. In parentheses are listed the mass fraction values for products, %. 2. In the denominator are presented data calculated from the additivity.

of the residue of lignine thermal destruction, increases at 350 °C. As the process temperature increased the lignine conversion level, on the contrary, decreases exhibiting a negative value at 400 °C.

The observed effect of the increase in the yield of total distillate products is determined mainly by a rise in the yield of hydrocarbonic distillate products resulting from tar and, to all appearance, is caused by the fact that free radicals are formed due to the thermal dissociation of weak chemical bonds in the structure of lignine which radicals initiate the reactions of liquid-phase cracking of the petroleum residue. A similar effect was observed by the authors of [17, 18] for the process of joint pyrolysis of biomass (lignine) with polyolefines. Earlier the initiating influence of lignine adding on the braking of aliphatic carbon-carbon bonds in coal macromolecules during the processes of liquefaction has been established in [19−21]. The authors of these works assumed that the thermal depolymerization of lignine within the temperature range of 300−400 °C results in the formation of phenoxy radicals those could enter into reactions with coal.

The petroleum residue influences also the yields of the products of lignine thermal destruction. The decrease in the yield of gaseous products in the joint process is, to all appearance, determined by a decrease in the level of lignine conversion into low-molecular thermal destruction products. The decrease in the apparent conversion level of lignine with the process temperature rising could be explained by an increased formation rate for high-molecular condensation products from tar on the reactive surface of the solid lignine thermal destruction product, in a similar manner as presented in [11].

In order to study the influence of the ratio lignine: petroleum residue and of the joint process time upon the yield of the top hydrocarbonic layer of distillate products we carried out the experiments with another example of petroleum residue such as bitumen. Bitumen contains a lower amount of low-molecular components as compared to tar, therefore the percentage of compounds formed due to thermal cracking of the petroleum product is higher in distillate products comparing with the low-molecular components forerunning from it.
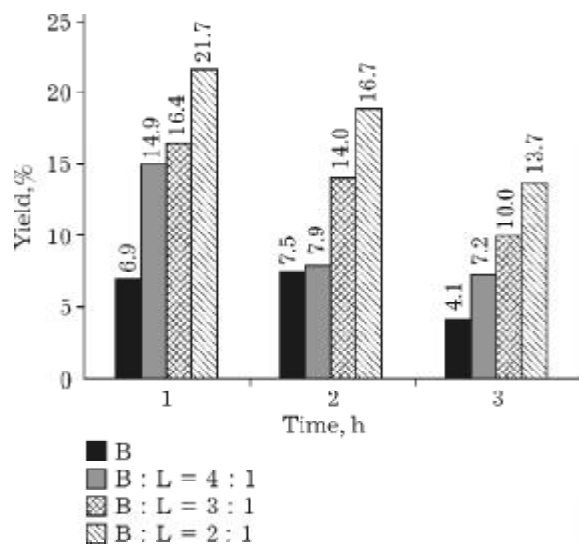
Fig. 1. Yield dependence on B: L ratio and on the processing time for the top hydrocarbonic layer of distillate products formed via the thermal destruction of bitumen (B) and its mixtures with lignine (L)
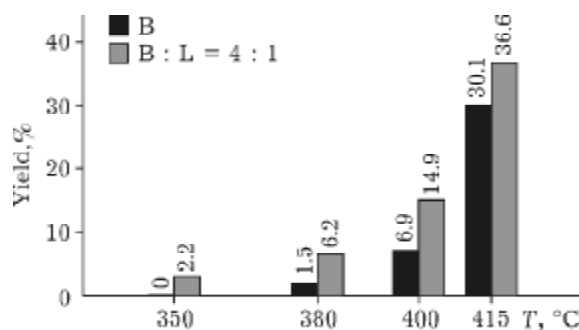

Fig. 2. Temperature dependence for the yields of the top hydrocarbonic layer of distillate products formed via bitumen thermal destruction (B) and its mixtures with lignine (L) during 60 min.

Figures 1, 2 display the yield dependences on bitumen/lignine ratio, process duration and temperature for the top hydrocarbonic layer of distillate products formed *via* thermal destruction of bitumen and its mixtures with lignine.

Much more pronounced promoting effect of lignine adding is observed within the first hour of the process: for this time the evolution of the distillate products formed due to lignine thermal destruction (bottom layer of the products) is almost finished. With the increase in the duration of the process the accumulation rate for the top layer of distillate products resulting from the mixture decreases, but it is still considerably exceeding the rate of the formation of distillate products those result from the only bitumen thermal cracking. With the increase in the content of lignine in the mixture the yield of the top layer of distillate products increases.

Investigation of the products

Cracked residue in the reactor. In the case of the thermal cracking of the only tar during 60 min a small amount of toluene insoluble substances observed is formed in the cracked residue only at temperature of 400 °C and higher (see Table 1). As the consequence, the toluene insoluble substances isolated through the extraction of the cracked residue from the pyrolysis of tar and lignine mixture represent mainly the residue of lignine thermal destruction and the products of the polymerization tar components on the lignine surface.

The results of the elemental analysis of initial lignine, cracked residue of lignine pyrolysis

TABLE 2

Elemental analysis data for initial lignine and toluene insoluble substances of cracked residue

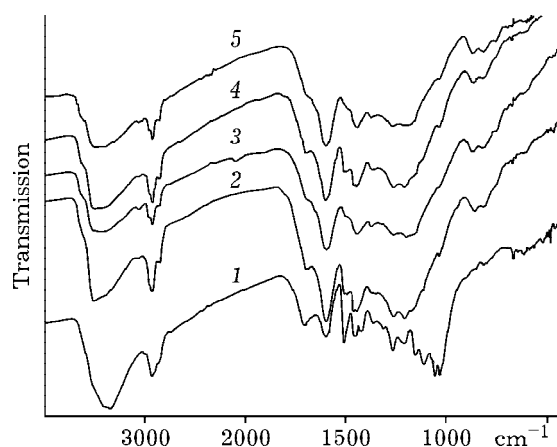| Experimental conditions	Mass fraction, %				H/C	O/C
	C	H	N	O		
Initial lignine	59.4	6.4	0.2	34.0	1.29	0.43
Lignine, 350 °C	74.0	4.7	−	21.3	0.76	0.22
Tar : Lignine = 3 : 1, 350 °C	74.6	4.8	−	20.6	0.77	0.21
Lignine, 380 °C	75.1	4.8	−	20.1	0.77	0.20
Tar : Lignine = 3 : 1, 380 °C	76.2	4.1	−	19.7	0.65	0.19
Lignine, 400 °C	75.6	4.5	−	19.9	0.71	0.20
Tar : Lignine = 3 : 1, 400 °C	78.5	4.6	−	16.9	0.70	0.16

Fig. 3. IR spectra of the initial лигнина (*1*) and toluene insoluble substances, isolated from the cracked residues obtained via lignine thermal destruction at 350 (*2*) and 400 °C (*3*) and those from lignine mixture with tar (1 : 4) thermal destruction at 350 (*4*) and 400 °C (*5*).

of the initial lignine, according to data presented in [5, 22, 23], exhibit the characteristic bands inherent in the vibration of the aromatic rings at the wavenumbers of 1600 and 1510 cm^{-1}, the C–H bonds at 2850–3060, 1362 and 1452 cm^{-1}, the carbonyl oxygen at 1707 cm^{-1}. Furthermore, there is a wide absorption band related to O–H bond vibration with the maximum at 3504 cm^{-1}, C–O bond vibration in aliphatic O–H groups at 1033 cm^{-1} as well as a number of absorption bands related to the C–O and C–O–C bonds vibration in ethers and phenols within the range of 1058–1280 cm^{-1} among those one could recognize a band related to C–O bond vibration in the guaiacyl group at 1267 cm^{-1}.

The IR spectra of the residues of lignine pyrolysis obtained at the temperature of 350 and 400 °C show the carbonyl oxygen vibration band at 1707 cm^{-1} to disappear, the absorption intensity of aliphatic O–H groups at 1033 cm^{-1} and of hydroxyl groups within the wave number range of 3300–3550 cm^{-1} to decrease profoundly as well as the band intensity of the aromatic ring vibrations at 1598 cm^{-1} to increase considerably. The presence of the absorption band at 1264 cm^{-1} in the IR spectra of the lignine pyrolysis residue indicates the conservation of the guaiacyl group structures occurring therein.

The IR spectra of the solid residue of joint pyrolysis at 350 and 400 °C to an insignificant extent differ from the IR spectra of the lignine thermal destruction residue. One could note that there is a somewhat higher intensity of the absorption bands at 3040, 1600 and 756 cm^{-1} those are related, apparently, to aromatic structures formed resulting from the reactions of petroleum residue components on the surface of the lignine pyrolysis residue.

and toluene insoluble substances of cracked residue from joint process are presented in Table 2.

The residue of lignine thermal destruction is characterized by a higher content of carbon and a lower content of hydrogen and oxygen in comparison with the initial lignine. The elemental compositions of both the residue of the only lignine pyrolysis and toluene insoluble substances in the isolated from the cracked residue of the joint process at 350 °C, are almost identical. At the temperature of 380 and 400 °C the H/C and O/C ratio values for toluene insoluble substances obtained in the joint process are lower than the ratio values for the residue of lignine pyrolysis.

Figure 3 demonstrates IR spectra of the initial lignine, of the residue of lignine pyrolysis and of toluene insoluble substances from the cracked residue of the joint process. IR spectra

TABLE 3

Characteristics of toluene soluble products of the cracked residue

Experimental conditions	Temperature, °C	H/C	Hydrogen distribution (according to ^{1}H NMR), %				
			H_γ	H_β	H_α	H_{ol}	H_{ar}
			0–1 ppm	1–2 ppm	2–4.5 ppm	4.5–6.7 ppm	6.7–10 ppm
Initial tar	–	1.57	19.2	63.5	13.5	–	3.8
Tar	380	1.00	11.6	43.0	26.7	2.4	16.3
Tar : lignine = 3 : 1	380	1.40	16.4	57.4	16.4	1.6	8.2
Tar	400	0.98	11.6	45.3	23.3	1.2	18.6
Tar : lignine = 3 : 1	400	1.20	15.9	58.7	17.5	–	7.9

TABLE 4

Elemental analysis data for liquid products of lignine pyrolysis and for joint process distillate products bottom layer

Experimental conditions	Temperature, °C	H/C	Mass fraction, %			
			C	H	N	S + O
Lignine	350	1.56	71.6	9.3	–	19.1
Tar : Lignine = 3 : 1	350	1.43	66.9	8.0	0.2	24.9
Lignine	380	1.46	69.7	8.5	–	21.8
Tar : Lignine = 3 : 1	380	1.30	68.6	7.4	0.2	23.8
Lignine	400	1.40	71.2	8.3	–	20.5
Tar : Lignine = 3 : 1	400	1.38	67.1	7.7	0.2	25.0

The results of the investigation of the toluene soluble part of cracked residue from tar thermal destruction and from the joint process using the methods of elemental analysis and ^{1}H NMR spectrometry are presented in Table 3.

Comparing to the initial tar the cracked residue of tar pyrolysis demonstrates a lower ratio H/C and, according to the data of ^{1}H NMR, a higher content of the aromatic hydrogen (H_{ar}) and hydrogen in α-position to the aromatic ring (H_α). For the joint process the H/C ratio in toluene soluble products increases, whereas the values of H_{ar} and H_α considerably decrease. Taking into account the fact that the main part of these products is presented by tar compounds, the results obtained could be explained as it follows: free radicals formed due to the thermal decomposition of lignine at 380 and 400 °C initiate the reactions of polymerization and condensation of petroleum residue asphaltenes containing aromatic structures, with the formation of insoluble products, "coke" [11]. As the result of this process, an increase in the percentage of compounds with a lower aromaticity is observed for the solution.

The IR spectra for toluene soluble products of tar thermal destruction and joint process cracked residue are presented in Fig. 4. One can see that the IR spectra of joint process products demonstrate an onset of the carbonyl group absorption band at 1690 cm^{-1} and an increase in the absorption intensity at 3400 and 3500 cm^{-1} due to a small amount of compounds passed from lignine into the solution.

Bottom layer of distillate products. Table 4 displays the results of the elemental analysis of the bottom layer of the distillate products formed in the pyrolysis of lignine and its mixes with tar. The H/C ratio in the products of joint process appeared lower, whereas the content of oxygen was higher in comparison with the corresponding data for the products of pyrolysis of the only lignine. To all appearance, this fact is connected with the transfer of compounds with a high percentage of aliphatic groups formed from lignine out of the bottom layer towards the top hydrocarbonic layer. The ^{1}H NMR spectrometry data corroborate our assumption. So, the ^{1}H NMR spectra of the bottom layer of joint process products (Fig. 5) exhibit a considerable decrease in the relative intensity of aliphatic hydrogen absorption within the range of 0–2 ppm, whereas an increase is observed for the absorption of the aromatic hydrogen (6.7–10.0 ppm) as well as of the hydrogen in α-position with respect to the aromatic ring and in α-position to the oxygen atom (2–4.5 ppm). The signal from the methoxy groups is observed
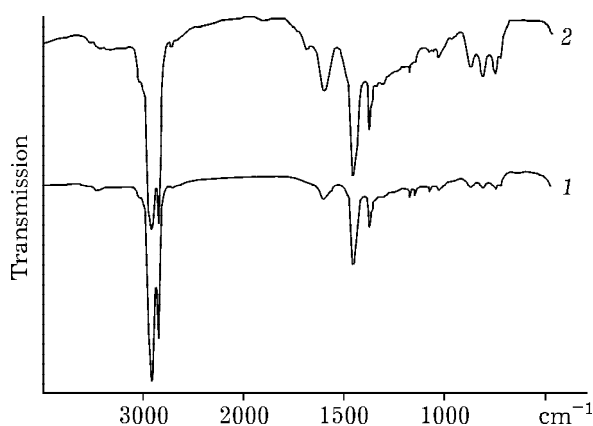

Fig. 4. IR spectra of toluene soluble substances isolated from the cracked residue obtained *via* the thermal destruction of tar at 350 °C (*1*) and of tar mixture with lignine (1 : 4) at 380 °C (*2*).
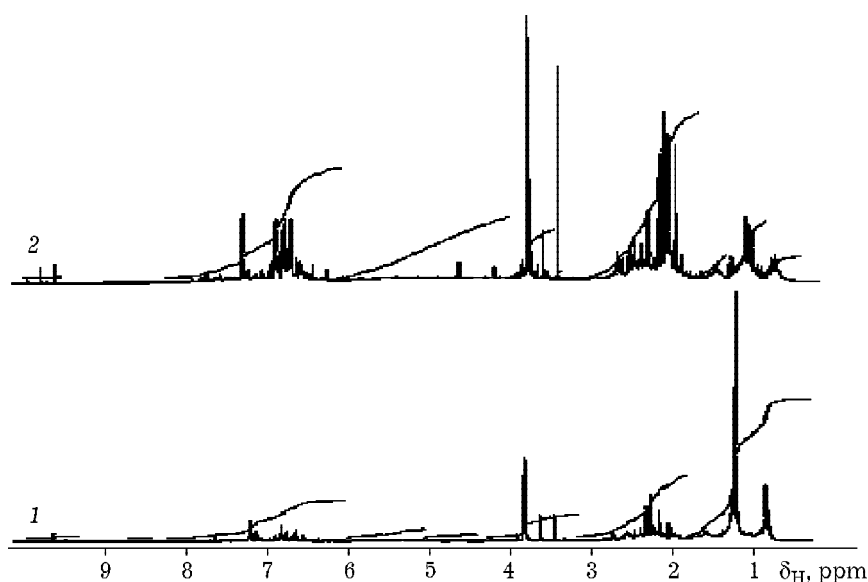
Fig. 5. ^{1}H NMR spectra of the bottom layer of distillate products obtained *via* the thermal destruction of lignine (*1*) and of its mixtures with tar (1 : 4) at 400 °C (*2*).
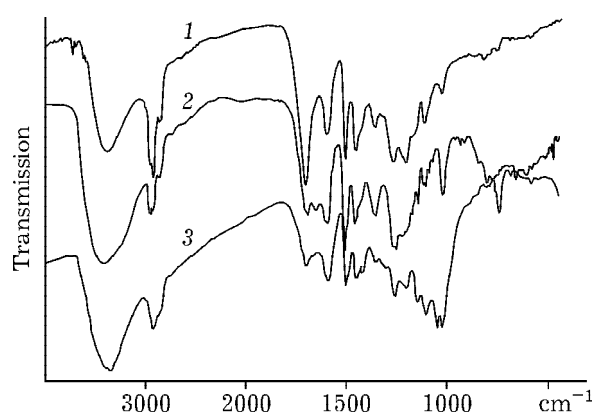

Fig. 6. IR spectra of the initial lignine (*1*), tar and lignine mixture (1 : 4) at 400 °C (*2*) and the bottom layer of distillate products obtained *via* lignine thermal destruction at 400 °C (*3*).

within the range of 3.6–3.8 ppm. IR spectra of the initial lignine and bottom layer of distillate products (Fig. 6) exhibit characteristic absorption bands common to both systems inherent in the OH groups (within the range wave number range of 3200–3500 and 1026–1270 cm^{-1}), the carbonyl groups (1703–1707 and 1666 cm^{-1}), the aromatic rings (1600, 1500–1515 cm^{-1}), the guaiacyl structures (1267 cm^{-1}). The IR spectra of the products also demonstrate a strong absorption of the aromatic hydrogen in the *ortho*-substituted benzene rings (748 cm^{-1}).

Top layer of distillate products. Table 5 demonstrates the results of the elemental analysis and hydrogen distribution according to ^{1}H NMR spectra of the distillate products of tar thermal cracking as well as of joint process. IR

TABLE 5

Characteristics of tar thermal cracking distillate products and of joint process distillate products top layer

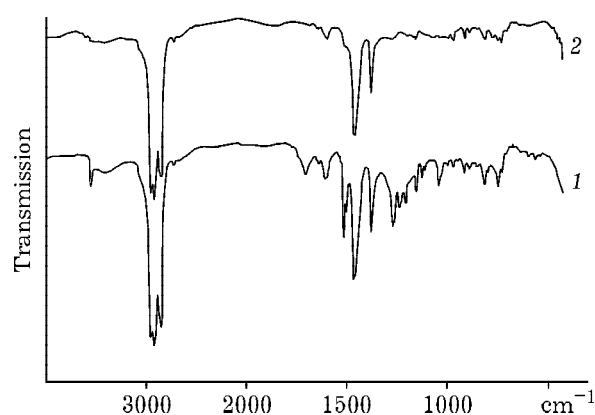| Experimental conditions	Temperature, °C	H/C	Hydrogen distribution (according to ^{1}H NMR), %				
			H_γ	H_β	H_α	H_{ol}	H_{ar}
			0–1 ppm	1–2 ppm	2–4.5 ppm	4.5–6.7 ppm	6.7–10 ppm
Tar	350	1.78	17.9	66.0	12.5	–	3.6
Tar : lignine = 3 : 1	350	1.76	22.2	57.8	13.3	–	6.7
Tar	380	1.79	27.8	55.5	11.1	2.8	2.8
Tar : lignine = 3 : 1	380	1.80	22.7	56.8	13.6	2.3	4.6
Tar	400	1.82	23.8	57.1	11.9	2.4	4.8
Tar : lignine = 3 : 1	400	1.93	24.4	56.1	12.2	2.4	4.9

Fig. 7. IR spectra of the top layer of distillate products obtained *via* thermal destruction of lignine and tar mixture (1 : 4) at 400 °C for 60 min of the reaction (*1*) and for the last of 20 min of the reaction (*2*).

spectra of these products are presented in Fig. 7. The distillate products of tar thermal cracking consist of aliphatic compounds, including compounds with the aromatic and olefinic groups, which is in a good agreement with the data presented in [13, 15, 16]. The products of tar thermal cracking also form a great deal of the top layer of the joint process distillate products. All the products contain long alkyl chains ($>C_4$), which is indicated by the absorption band at the wave number of 724 cm^{-1}. Besides, there are weak absorption bands of the carbonyl groups (1710 cm^{-1}) as well as of the benzene (1515 cm^{-1}) and guaiacyl rings (1270 cm^{-1}) observed in the IR spectra of the joint process products, especially at short reaction time (20 min). This fact indicates the presence of aliphatic groups (to all appearance, with a high percentage) within the top layer of the compounds formed from lignine.

Figure 8 demonstrates chromatography profiles for the distillate products of bitumen pyrolysis as well as for the top layer of the distillate products of bitumen and lignine joint pyrolysis of at 415 °C. The products of bitumen pyrolysis and the products of the joint pyrolytic process exhibit a qualitatively identical hydrocarbonic composition. The most pronounced peaks in the chromatograms are conforming to normal alkanes whose retention time values are somewhat lower as compared to the retention time values for corresponding olefines. Furthermore, the products contain isoparaffines [16].

Table 6 displays the quantitative data calculated from chromatographic profiles concerning the content of C_5-C_{10}, $C_{11}-C_{15}$ и $C_{16}-C_{30}$ hydrocarbonic fractions in the distillate products obtained in the process of bitumen pyrolysis at 400 and 415 °C for different reaction time. The margins of the fractions were determined basing on the retention time values for normal alkanes. The products of bitumen pyrolysis at 400 °C predominantly contain C_5-C_{10} fraction and an insignificant percentage (up to 3.1 %) of $C_{16}-C_{30}$ fraction. With the increase in the reaction time the content of $C_{11}-C_{15}$ fraction increases (from 21.8 up to 37.0 %) due to a decrease in the percentage of the C_5-C_{10} fraction. As the temperature rising up to 415 °C the percentage of the C_5-C_{10} fraction decreases, the content of the $C_{11}-C_{15}$ fraction almost does not change, and the percentage of the $C_{16}-C_{30}$ fraction increases.

TABLE 6

Group composition of the fractions of distillate products obtained *via* bitumen pyrolysis

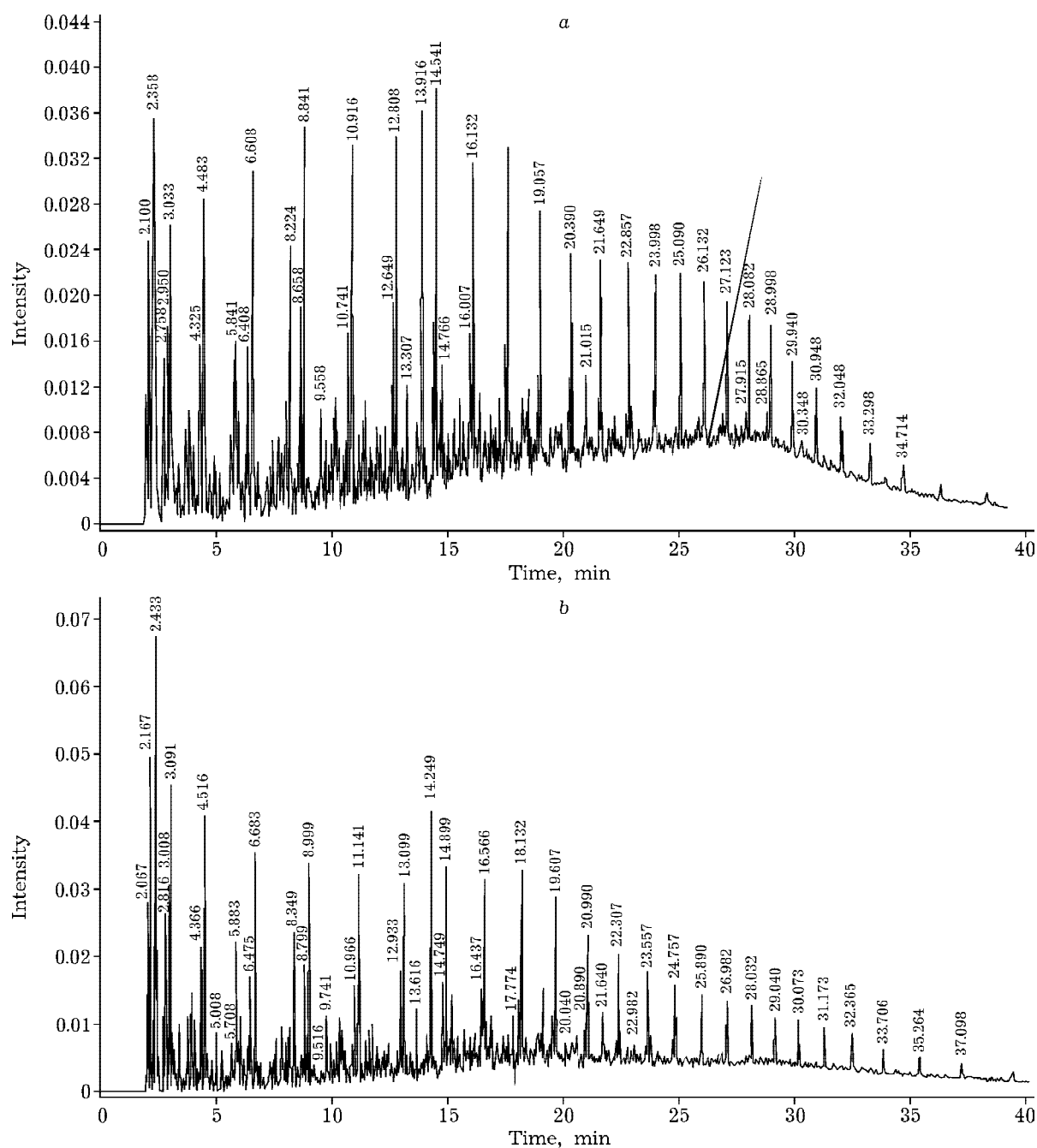| Temperature, °C	Reaction time, min	Group composition, %		
		C_5-C_{10}	$C_{10}-C_{20}$	$C_{20}-C_{30}$
<400	0	–	–	–
400	0–20	75.8	21.8	2.5
400	20–40	67.1	31.2	1.7
400	40–60	59.9	37.0	3.1
<415	0	66.4	28.1	5.5
415	0–20	51.4	34.3	14.3
415	20–40	49.3	32.0	18.7
415	40–60	48.9	33.3	17.7

Fig. 8. Chromatographic profiles of the distillate products of bitumen pyrolysis (*a*) and of the top layer of distillate products of bitumen and lignine joint pyrolysis (*b*) obtained at the temperature of 415 °C.

Table 7 demonstrates data concerning the content of C_5-C_{10}, $C_{11}-C_{15}$ и $C_{16}-C_{30}$ fractions in the distillate products obtained due to joint pyrolysis of bitumen and lignine for different reaction time within the temperature range of 380–415 °C.

At short reaction time when lignine exerts a pronounced activation effect, for the distillate products of the pyrolysis of the bitumen : lignine (4 : 1) mixture at 400 and 415 °C the per-centage of $C_{16}-C_{30}$ fraction is higher, whereas the percentage of C_5-C_{10} fraction is lower in comparison with those for distillate products of bitumen. At the same time the differences in the content of $C_{11}-C_{15}$ fraction are insignificant. With the increase in temperature from 380 up to 415 °C for the mixture, as well as for the only bitumen, an increase in the content of $C_{16}-$ C_{30} fraction is typically observed due to the re-

TABLE 7

Group composition of the fractions of top layer distillate products obtained *via* bitumen and lignine joint pyrolysis

Bitumen/Lignine ratio	Temperature, °C	Reaction time, min	Group composition, %		
			C_5-C_{10}	$C_{10}-C_{20}$	$C_{20}-C_{30}$
4 : 1	<380	0	38.6	42.8	18.6
	380	0−20	70.0	28.1	1.9
	380	20−40	76.2	23.2	0.6
	380	40−60	61.4	36.5	2.1
4 : 1	<400	0	48.3	40.2	11.5
	400	0−20	52.9	35.7	11.4
	400	20−40	48.7	42.3	9.0
	400	40−60	55.1	36.5	8.4
4 : 1	<415	0	42.1	36.5	20.4
	415	0−20	46.6	31.6	21.8
	415	20−40	43.1	32.7	24.2
	415	40−60	37.1	28.9	34.0
3 : 1	<400	0	34.3	41.5	24.2
	400	0−20	50.0	33.2	16.8
	400	20−40	53.3	37.0	9.7
	400	40−60	53.5	40.4	6.1

duction of the percentage of C_5-C_{10} fraction. These regularities are also traced for the mixture with the bitumen : lignine ratio equal to 3 : 1. Thus, the addition of lignine to bitumen influences the composition of hydrocarbonic distillate products of its pyrolysis in a similar manner as the increase in the process temperature resulting in an increase in the content of high-boiling fractions. The increase in time of the joint process results in lowering the activation effect of lignine addition. Moreover, as to compare with initial bitumen, the composition of the cracked residue in the reactor changes to a considerable extent, too; this affects the ratio between hydrocarbonic fractions.

CONCLUSION

Basing on the data obtained concerning the composition of the products of the joint thermal processing of lignine and petroleum residue the pathways are proposed for their practical. The top hydrocarbon layer could be used for obtaining fuel products by means of hydrogenation processing, in much the same manner as the distillate products of joint thermal cracking of oil stock with shale [24] and other reactive additives [25]. The bottom layer of the distillate products could find application as a chemical phenol-containing raw material [4, 6] and in the manufacture of phenolic resins [26, 27].

The parameters for the joint processing of lignine and petroleum residue can be matched in such a way as the thermal cracked residue representing a modified bitumen product to be discharged out of the reactor in the liquid form. The residue contains the particles of carbonized lignine, the liquid fraction of the residue is modified with high-boiling products of lignine thermal destruction. Our preliminary studies have demonstrated the possibility of using the cracked residue of the joint process as a bituminous binding agent for road-building with the properties improved in such parameters as the frost resistance and the adhesion with respect to mineral filler materials. The use of products of lignine and petroleum residue joint heat treatment in road-building is considered in [28], and the influence of active coal additives obtained from vegetative raw material, upon the properties of paving bitumen is studied by the authors of [29].

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