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Analysis and Processing of Heavy Pyrolysis Tar

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Abstract

Chemical composition of the light fraction ($T_{\text{boil}} \leq 300$ °C) of heavy pyrolysis tar (HPT) was studied; more than 40 components were identified. The content and nature of the still bottoms of HPT were determined. It was established that the method of HPT processing is determined mainly by the concentrations of naphthalene, unsaturated compounds and still bottoms. The processes of HPT polymerization with the application of radical type initiators dicumyl peroxide and di-*tert*-butyl peroxide (DTBP) were studied. New grades of petroleum polymer resins (PPR) with high softening temperature were developed; they can be used in rubber-processing industry. A method of HPT processing using the still bottoms of styrene rectification and DTBP, followed by evaporation of volatile components, was proposed for obtaining PPR with required properties and the yield up to 68 %.

Key words: heavy pyrolysis tar, chromatographic analysis, chemical composition, processing technology, radical polymerization, dark petroleum polymer resin

INTRODUCTION

Heavy pyrolysis tar (HPT) is formed as a side product of ethylene production. According to the data of 2010, up to 40 thousand t of HPT were obtained at three plants of Sibur Holding OJSC (EP-60 SIBUR-Khimprom JSC, EP-300 Tomskneftekhim Ltd., and EP-300 SIBUR-Neftekhim OJSC). Heavy pyrolysis tar is a viscous dark liquid with naphthalene odour, readily soluble in aromatic hydrocarbons and chlorinated compounds. The major components of HPT are bi-, tri- and polycyclic aromatic hydrocarbons (58–88 %), tar and pyrobitumen (11–34 %) [1].

At present HPT is used mainly for the production of soot and technical carbon [2–4] due to the high concentration of polycyclic aromatic hydrocarbons and low sulphur content. In addition, a trend of weighting of pyrolysis raw material is observed because heavy oil mixtures are involved in processing (gas-oil stock, black oil, oil tar), which causes an increase in the yield of HPT. This fact defines the necessity to process HPT into commercial products.

Considering the methods of HPT processing, it is necessary to take into account its characteristics: stillage bottoms content, concentrations of naphthalene and sulphur; component composition of the light fraction of HPT, which is a mixture of low-molecular mass compounds with boiling temperature up to 300 °C.

EXPERIMENTAL

Thermal stability of HPT samples was studied by means of thermogravimetry (TG) with a TG 209 F1 Netzsch instrument within

TABLE 1

Conditions of the chromatographic analysis of HPT fractions

Parameters	Fraction No.		
	1	2	3
Evaporator temperature, °C	280	300	320
Initial temperature, °C	50	70	90
Final temperature, °C	290	290	290
Heating rate, °C/min	7	10	10
Exposure, min	5	5	5

temperature range 30–600 °C with the heating rate of 10 °C/min in argon atmosphere.

HPT separation into fractions was carried out by distilling under the following conditions. The 1st fraction: $P = 1$ atm; $T_{\text{vap}} = 57–75$ °C; yield: 3.55 %; the 2nd fraction: $P = 0.0227$ atm; $T_{\text{vap}} = 93–125$ °C; yield: 28.64 %; the 3rd fraction: $P = 0.01974$ atm; $T_{\text{vap}} = 128–135$ °C; yield: 10.46 %; the 4th fraction (stillage bottoms): $T_{\text{vap}} > 135$ °C; yield: 57.36 %.

The composition and concentrations of tar components were determined by means of gas chromatography and mass spectrometry using an Agilent 7890A chromatographs equipped with MSD 5975C and FID. Analysis conditions: HP-5 (MS) column 30 m long, inner diameter 0.25 mm; analyser type: quadrupole; ionisation type: electron impact (EI) 70 eV (Table 1). The quantitative concentrations of components were determined using the internal standard; acetophenone was used as the latter.

^{13}C and ^{1}H NMR spectra were recorded with a Bruker Avance III 400 MHz spectrometer at room temperature using standard pulse programmes. The samples were dissolved in deuterated chloroform.

The IR spectra of stillage bottoms were recorded with a Varian Excalibur HE 3600 Fourier transform IR spectrometer with the resolution of 4 cm^{-1} with the help of the internal reflectance attachment within wavenumber range 4000–400 cm^{-1}. Polymerization of HPT was carried out in the presence of organic peroxide initiators: dicumyl peroxide (DCP) and di-*tert*-butyl peroxide (DTBP) under variation of the parameters of HPT polymerization.

The quality of the obtained petroleum polymer tar was estimated using the following physicochemical characteristics: softening point – according to Russian standard GOST 11506–73 (KiSh), ash value, acidity index – according to GOST 23955–80, bromine value – according to GOST 8997–89, volatile components content – according to GOST 7846–73.

RESULTS AND DISCUSSION

The samples of HPT collected at the plants of SIBUR Holding – Tomskneftekhim Ltd. (sample HPT-1), SIBUR-Neftekhim OJSC (sample HPT-2), SIBUR-Khimprom JSC (sample HPT-3) – were studied by means of chromatographic, spectroscopic and TG analysis methods.

It was established by means of TG that the major loss of HPT mass occurs in two stages (Fig. 1); the larger part (71–63 % of HPT mass) is evaporated within the range 70–130 °C and corresponds to the removal of the light fraction, the stillage bottoms account for 23–28 %. The maximal rate of HPT destruction is observed at a temperature of 380–390 °C. The residual mass, which is coked tar, at a temperature of 600 °C accounts for 6–9 %.

The quantitative content of more than 20 components was established by means of GC in HPT without preliminary separation of tar residue. However, it is necessary to stress that there are difficulties in interpreting the mass spectra of components due to their low content and low resolution of some chromatographic signals.

As a result of separation of the samples from high molecular mass components, the chromatograms exhibit a decrease of the back-

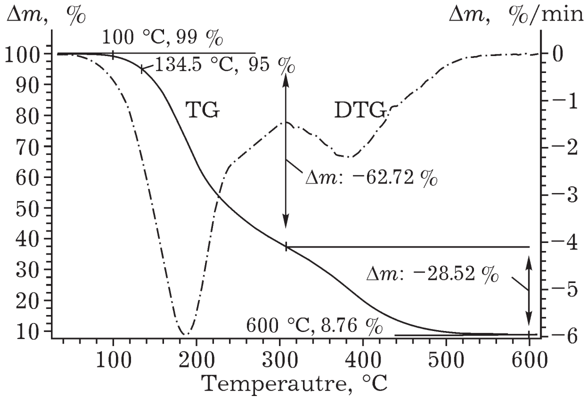

Fig. 1. Curves of mass loss (TG and DTG) for HPT-1 sample.

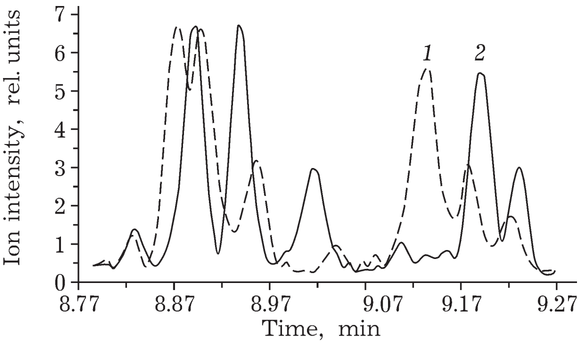

Fig. 2. Chromatograms of initial (*1*) and purified (*2*) fractions of HPT-2.

ground, improvement of the resolution of chromatographic signals, which allows us to identify a larger number of components and to determine the quantitative content of tar components more accurately (Fig. 2).

In order to confirm chromatographic data by means of ^{13}C NMR spectroscopy, the major tar components were identified on the basis of characteristic chemical shifts of the aromatic hydrogen atoms, ppm: naphthalene (125.7, 127.8 and 133.4), styrene (137.65, 136.98, 128.52, 127.78, 126.24, 113.70), diphenyl 140.8, 128.4, 126.9, 126.8) [5].

Additionally, more than 20 tar components were identified in the in het light fraction of HPT by means of GC-MS. The composition of HPT depending on manufacturer is shown in Fig. 3.

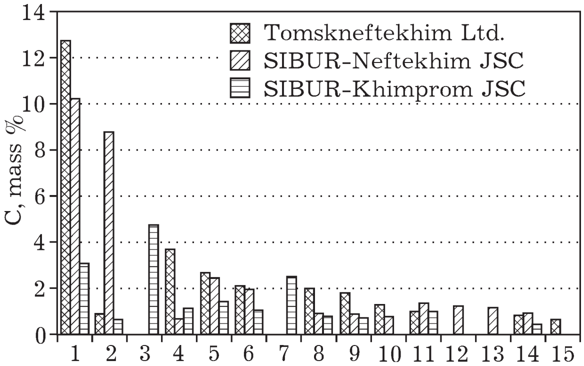

Fig. 3. Distribution of components in HPT from three manufacturers: 1 – naphthalene, 2 – diphenyl, 3 – 1,1-diphenylethane, 4 – indene, 5 – methylnaphthalene, 6 – 1-methylnaphthalene, 7 – styrene, 8 – 1-methyl-2-cyclopropene-1-yl-benzene, 9 – 2-methylindene, 10 – 1,4-dihydronaphthalene, 11 – phenanthrene and anthracene, 12 – 4-methyl-1,1′-diphenyl, 13 – 2- and 1-ethylnaphthalene, 14 – fluorine, 15 – hendecane.

Differences in the composition of different HPT samples are connected with the use of different initial raw materials and pyrolysis technologies. At Tomskneftekhim Ltd. and SIBUR-Neftekhim OJSC plants, the raw material for the production of ethylene is the straight-distillation petroleum fractions with the addition of a broad fraction of light hydrocarbons (BFLH), while at SIBUR-Khimprom JSC the raw material includes BFLH and liquefied hydrocarbon gases (LHG). In addition, there are some differences in the technology of pyrolysis at EP-300 and EP-60 installations. At SIBUR-Khimprom JSC they mix HPT with the stillage bottoms of styrene rectification (SBSR).

According to the results of thermal analysis, HPT is characterized by eth high content of stillage bottoms (about 40 %), which defines the necessity to study its composition.

According to the data of ^{13}C, ^{1}H NMR and IR spectroscopy, the stillage bottoms from HPT fractionation corresponds in the group composition to styrene-indene tar. At the same time, some differences are observed; they have decisive importance for the use of tar in corresponding areas of industry (Fig. 4). In particular, unsaturation of stillage bottoms is substantially higher than unsaturation of the similar samples of styrene-indene tar, which affects some of their technological characteristics.

Isolation of naphthalene in pure form is important direction of HPT processing because of the high naphthalene content (up to 13 %) and low content of diphenyl (less than 0.9 %); the latter hinders technological isolation of pure naphthalene due to the joint crystallization.

Obtaining PPT is considered as a promising direction of the use of HPT. Taking into account the fact that the yield of PPT is mainly affected by the content of stillage bottoms and unsaturated hydrocarbons [6, 7], HPT-1 sample was chosen as the initial raw material because it meets the major requirements: high content of stillage bottoms (about 40 %) and unsaturated hydrocarbons (about 10 %) that can participate in polymerization, polycondensation and compaction reactions.

Investigation of the methods of HPT processing includes selection of conditions providing the maximal yield of PPT. Tar of Pyroplast Polimer Plast with high softening temperature,

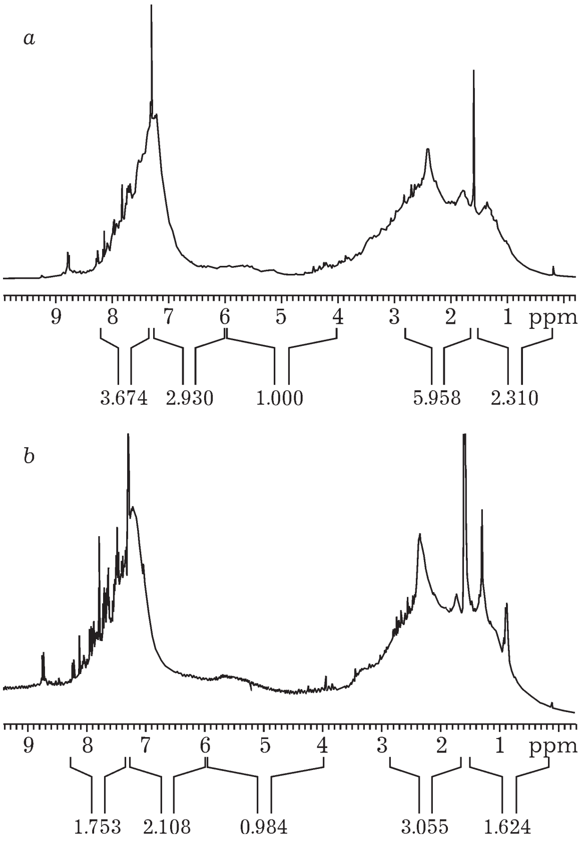

Fig. 4. ^{1}H NMR spectrum of stillage bottoms from HPT (*a*) and styrene-indene tar (*b*).

used as softener in rubber-processing industry, was chosen as a reference sample.

The method of HPT processing proposed by us is based on its separation leading to dark petroleum polymer tar and volatile aromatic components, and subsequent isolation of naphthalene.

The conditions of HPT processing are listed in Table 2.

The separation of HPT was carried out with the help of distillation under varied pressure. However, at technologically acceptable pressure of 0.3 atm, resulting PPT is characterized by the low yield (51 %) and low softening temperature (65 °C). The latter depicts the amount of residual volatile components, polymerization degree and cross-linking extent.

In this connection, HPT polymerization was carried out using radical initiators – DCP and DTBP – with the addition of the fraction containing substantial amount of unsaturated compounds (SBSR) varying polymerization temperature, amount of initiator and pressure during distillation.

An increase in polymerization temperature to 250 °C and amount of initiator to 2 m.f. in the presence of DCP provides acceptable PPT softening temperature and high product yield (64 %).

TABLE 2

Conditions of HPT processing

Exp. No.	Component ratio in reaction mixture, m.f.		Initiator type	T_p, °C	P, atm	PPT yield, %	T_{soft} (KiSh), °C
	SBSR	Initiator					
1	–	–	–	–	1.0	77	39
2	–	–	–	–	0.65	65	50
3	–	–	–	–	0.3	51	65
4	–	–	–	–	0.013	43	97
5	5	1	DCP	200	0.65	68	62
6	5	1	DCP	200	0.3	56	75
7	5	1	DCP	250	0.3	61	77
8	5	2	DCP	200	0.3	58	81
9	5	2	DCP	250	0.3	64	90
10	5	2	DTBP	120	0.3	56	85
11	5	2	DTBP	200	0.3	62	101
12	5	2	DTBP	250	0.3	68	110

Notes. 1. SBSR is stillage bottoms of styrene rectification; DCP is dicumyl peroxide, DTBP is di-tert-butyl peroxide; T_p is polymerization temperature; P is distillation pressure. 2. Dash means absence (evaporation of light components was carried out in experiments Nos. 1–4).

TABLE 3

Physicochemical characteristics of different samples of petroleum polymer tar (PPT)

Characteristics	PPT samples after evaporation of volatile components			Pyroplast
	from HPT without polymerization	from polymerizate with DCP	from polymerizate with DTBP	Polimer Plast
Softening temperature according to KiSh, °C	65	90	110	98
Mass concentration of ash, %	0.03	0.04	0.04	0.04
Mass concentration of total sulphur, %	0.20	0.18	0.12	0.10
Bromine value, g Br/100 g	34.4	29.9	24.5	23.9
Acid value, mg KOH/g	0.39	0.75	0.75	0.83
Mass concentration of volatiles, %	0.84	0.63	0.52	0.10

Polymerization in the presence of more active initiator – DTBP – causes an increase in the yield (up to 68 %) and an increase in PPT softening temperature (to 110 °C). Passing from DCP to DTBP for radical polymerization of HPT, unsaturation of PPT decreases by almost 20 %.

For the obtained PPT samples with maximal softening temperature, the major physicochemical parameters were determined: the mass concentration of ash, total sulphur and volatiles, bromine value and acid value. These characteristics of PPT samples obtained by us in comparison with the commercial sample Pyroplast Polimer Plast are presented in Table 3.

The use of the initiators of radical-type polymerization, in particular passing from DCP to DTBP. allows one to increase the yield of PPT and its softening temperature, and decrease unsaturation of PT.

CONCLUSION

Thus, on the basis of the data obtained on the composition of HPT, the methods of processing it are proposed. Among them, the most optimal one is polymerization using SBSR and DTBP, followed by evaporation of volatile components to obtain PPT with required properties with a yield up to 68 %.

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