

The Study of Tar Oxidation Process Kinetics of Paraffin Naphthenic Base with Activating Complex

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Abstract

Bitumen is a mixture of hydrocarbons and hetero-organic compounds of different structures with a complex chemical composition which conditioning its operational physico-chemical and mechanical properties. Also varying widely depending on the nature of bituminous materials and the technology of its processing. The tar of oil mixture from Romashkinsky and Kama region deposits owned by OJSC "Tatneft" was chosen as the raw material of the oxidation process. During the oxidation of heavy petroleum residues (HPR) a lot of reactions takes place simultaneously: dehydrogenation, dealkylation, oxidative polymerization, polycondensation, cracking, followed by "compaction" of its products caused by an increasing loss of hydrogen during oxidation, which in combination with the cyclization reactions leads to the formation of high molecular weight products of high aromaticity degree. Nowadays, the oxidation of heavy refinery residues by air is the main process of bitumen production in Russia. Various methods of oxidation process efficiency increase are developed, in particular, the increase of phase contact surface by improving the air supply devices, technological process optimization parameters, and the use of oxidation catalysts are known. The most promising area of oxidized bitumen production intensification and their quality improvement is the introduction to the oxidation process of various modifiers that change the dispersion state and the feedstock reactivity.

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1. Introduction

The tars of various oils, which are obtained by primary distillation of crude oil, cracked residues, the extracts selective oil refining, the asphalts of deasphalting process, fuel oils, pyrolysis process tars, etc. are used as the raw material of bitumen production in modern refineries. This leads to the need for an effective regulation of raw material properties and bitumen production process parameters with a given set of operating properties¹⁻⁵.

2. Experimental Part

The tar of oil mixture from Romashkinsky and Kama region deposits owned by OJSC "Tatneft" was chosen as the raw material of the oxidation process, the physico-chemical

properties of which are presented in Table 1^{4,6-10}. The activating complex^{10,11} is a multi-components system based on mixtures of carboxylic acids $C_{17}H_{33}COOH$, $C_{17}H_{31}COOH$, $C_{17}H_{29}COOH$ and polyhydric alcohols $C(CH_2OH)_4$, $C_3H_5(OH)_3$, and the catalyst containing manganese dioxide developing complex ethers and their salts, soluble in bitumen resins and providing a catalyzing effect on the kinetics of the oxidation process. The preparation of road bitumen was carried out in a laboratory unit of periodic action at the process temperature of 250 °C and air flow rate of 1.5-2 l/min per kg of raw material with periodic sampling during oxidation^{4,5,8}.

It should be noted that in order to obtain high-quality raw bitumen the residual raw material with a strictly determined composition is required, which satisfy the tars of heavy oils with naphthenoaromatic base containing

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a large amount of resin-asphaltene compounds with a low content of solid paraffins, the reserves of which are extremely limited in Russia. The selection of raw materials is conditioned by the expansion of the bitumen production resource base involving the tars with paraffin-naphthenic base (Table 1).

The group chemical composition of tar and its oxidation products, according to BashNII NP method is presented in Table 2. The method is based on the principle of liquid adsorption chromatography using the gradient displacement and the separation of heavy oil residue into seven groups: paraffin-naphthenic hydrocarbons; monocyclic, bicyclic, polycyclic aromatic hydrocarbons, forming a total group of oils; benzene, alcohol-benzene resins or resins 1 and resins 2; asphaltenes⁹.

After the oxidation for two hours, the decrease of paraffinic naphthenic and aromatic hydrocarbons content is observed compared to the original tar. Thus there is a slight increase in the content of light and middle aromatic hydrocarbons. At a further oxidation for more than ten hours, a marked increase in the concentration of asphaltenes and the reduction of mono- and bicyclic aromatic hydrocarbons in bitumen takes place, compared to the initial tar and its two hour oxidation product. It is interesting, that the content of benzene resins varies slightly, while alcohol-benzene resins are increased by almost 1.5 times. During the oxidation of tar the content

of heavy aromatic hydrocarbons is reduced drastically, while the concentration of asphaltenes in the bitumen after two hours of oxidation increases evenly. Thus, during the oxidation an even concentration in the bitumen of aromatic and paraffin-naphthenic hydrocarbons is observed: a slight decrease of mono- and bicyclic - and the sharp increase of polycyclic hydrocarbons. Along with this, a slight increase in tar content takes place, especially of alcohol-benzene ones for ten hours of oxidation.

One may conclude on the preferential conversion of resins and oils in asphaltenes by oxidation, as the increase in the content of the latter is accompanied by the change in the concentration of the first ones. However, it is difficult to determine a transition method for sure: either the oils are directly converted into asphaltenes during oxidation process, or their transition into asphaltenes is performed through the formation of tars. Apparently, this issue may be resolved after detailed kinetic studies.

Possibly, the oxidation process is accompanied not only by the enlargement of molecules but also by the destruction of either original products or the intermediate products formed during the oxidation. This is evidenced by a sharp increase (about 1.5 times) of light and medium aromatics. The behavior of alcohol-benzene resins is equally specific in this respect.

The introduction of activating complex in the oxidation process at the amount of 6% wt. in raw material leads to important results: the modifier is distributed mainly in the medium aromatic (bicyclic) hydrocarbons and alcohol-benzene hydrocarbons of original tar (Table 3). A high rate of tar oxidation using a modifying additive to reduce the time of oxidation by 60-70% should be noted. The decrease of all oil hydrocarbons, including all their constituent structures, with a notable reduction of heavy aromatic hydrocarbons almost two times is observed during the oxidation. So, for example, for the first six hours of oxidation without the addition in tar the polycyclic aromatic hydrocarbons are reduced by 15.6% wt. with the modifier - by 23.2 % wt. Bicyclic aromatic hydrocarbons are changed by waves in two cases. The content of monocyclic aromatic hydrocarbons is changed slightly. For three hours of oxidation with a modifying additive the content of paraffin-naphthenic hydrocarbons content is reduced to 3.4% wt. and for six hours to 6.5% wt. without the modifier for 2.8 wt. and 3.8 wt.

These results show that in the presence of an activating complex of paraffinic naphthenic hydrocarbons the con-

Table 1. Physico-chemical properties of tar

Index name	Tar mixture of Romashkinsky and Kama region oil fields
Density at 20 °C, kg/m ³	987,8
Relative viscosity at 80 °C, RV	27,1
Total sulfur content, % wt.	0,887
Coking ability, % wt.	8,3
Group chemical composition, % wt.:	
of oils, including	76,00
-paraffin-naphthenic	20,80
-monocyclic	14,20
-bicyclic	6,40
-polycyclic	34,60
Resins, including	18,00
benzene resins	6,60
alcohol-benzene resins	11,40
asphaltenes	5,80

Table 2. Group chemical composition of tar and its oxidation products

Oxidation period, hours	Oils				Tars		Asphaltenes
	Paraffin-naphthenic hydrocarbons	Monocyclicaromatic hydrocarbons	Bicyclicaromatic hydrocarbons	Polycyclicaromatic hydrocarbons	Benzene	Alcohol-benzene	
Tar	20,8	14,2	6,4	34,6	6,6	11,4	5,8
2	18,1	20,2	10,2	22,8	7,2	13,7	7,8
6	17,7	17,8	9,4	21,5	7,5	14,7	11,4
10	17,3	15,4	8,6	20,2	7,8	15,7	15,0
18	14,5	12,0	6,0	16,2	8,0	16,7	26,6
24	13,9	10,9	4,5	12,9	8,2	17,5	32,1

Table 3. Group chemical composition of tar and its oxidation products with modifying additive

Oxidation period, hours	Oils				Tars		Asphaltenes
	Paraffin-naphthenic hydrocarbons	Monocyclicaromatic hydrocarbons	Bicyclicaromatic hydrocarbons	Polycyclicaromatic hydrocarbons	Benzene	Alcohol-benzene	
Гудрон	20,8	14,2	6,4	34,6	6,6	11,4	5,8
Гудрон+М, 200 °С	19,2	14,4	9,9	25,4	6,0	18,5	6,6
Гудрон+М, 250 °С	18,5	9,7	6,7	25,4	6,7	22,0	11,0
1	19,9	16,3	4,9	24,4	7,9	20,5	6,1
3	17,4	11,3	5,9	17,6	6,6	27,2	14,0
5	16,7	11,9	6,5	16,9	8,0	26,2	13,8
6	14,3	5,2	5,1	6,2	6,6	28,4	34,2
7	11,7	11,9	8,7	9,0	8,6	31,5	18,6

version takes place much faster and their relative contents in oils and resins decreases. At the same time there a sharp increase of resins and asphaltenes takes place. The new formation of asphaltenes is observed especially clearly: in the presence of an activating complex by 28.2% wt. of pure tar at 12.5% wt. An image of hydrocarbon group conversion vector, as the transition of low molecular weight into high molecular weight requires a clearing: under certain conditions, a reverse process of high and low molecular weight compounds is possible with their subsequent conversion back into the heavier components, i.e. during the oxidation of tar the cyclic processes of hydrocarbon group interconversion take place. This is supported by the fact that a relatively constant degree of

condensation of the heaviest components - asphaltenes and its independence from both the duration of oxidation and on the presence of various additives was shown by special experiments.

Based on the analysis of the group chemical composition of tar oxidation without an activating complex (Table 2), the first six hours, and the process takes place mainly towards the accumulation of resins due to the oxidation of oils, resulting in only during the 8-th hour and its relative content of asphaltenes grows at further oxidation. An activating system allows to reduce not only the content of paraffin-naphthenic hydrocarbons due to the destruction of high-molecular normal paraffins to shorter chains, but also to increase the yield of asphaltenes without a long-

term accumulation of resins. Besides, we assume that the polycyclic naphthenes with lateral alkyl substituents contained in paraffin-naphthenic hydrocarbons of oils are turned likely into benzene resins.

The early studies determined that the group chemical composition in the oxidation process changes and is not always clearly related to the qualitative characteristics of bitumen¹²⁻¹⁴. It is possible that one of the reasons for this are the structural features of raw materials and the products of its oxidation composition. The structural

changes during the oxidation may be observed on the basis of quantitative changes in the content of structural fragments. For this purpose, infrared Fourier spectroscopy method was used for the analysis of tar and its oxidation products with a modifying additive. The spectral ratios determined by the ratio of the absorption bands at different frequencies, using a baseline in the range of 1850 - 650 cm⁻¹ IR - spectrum (Table 4 and 5) were calculated for the evaluation of structural group content.

Table 4. The change of structural-group composition of tar and its oxidation products with an activating complex

Oxidation period, hours	CH ₂	CH ₃	C=C _{arom.}	C=O _{ethers}	C=O _{acids}	SO
Tar	0,13	0,53	0,14	0,02	–	0,08
Tar+ M, 200 °C	0,14	0,54	0,23	1,25	0,34	0,11
Tar+ M, 250 °C	0,15	0,54	0,27	0,20	0,10	0,10
1	0,16	0,56	0,32	0,21	0,10	0,13
2	0,18	0,62	0,36	0,24	0,12	0,13
3	0,16	0,57	0,32	0,22	0,11	0,13
4	0,18	0,61	0,39	0,10	0,12	0,16
5	0,17	0,65	0,41	0,17	0,15	0,17
6	0,15	0,62	0,39	0,15	0,13	0,15
7	0,14	0,58	0,36	0,13	0,12	0,12

Table 5. Calculated ratios of structural-group composition of tar and its oxidation products with an activating complex

Oxidation period, hours	Alifaticity	Oxidation		Branching	Paraffin structure share	Condensation degree
		C=O/C=C _{arom.}	SO/C=C _{arom.}			
Tar	4,71	0,14	0,57	4,08	0,66	0,62
Tar + M, 200°C	2,96	6,9	0,48	3,86	0,68	1,24
Tar + M, 250°C	2,56	1,11	0,37	3,60	0,69	1,36
1	2,25	0,97	0,41	3,50	0,72	1,55
2	2,22	1,00	0,36	3,44	0,80	1,48
3	2,28	1,03	0,41	3,56	0,73	1,50
4	2,03	0,56	0,41	3,39	0,79	1,58
5	2,00	0,78	0,41	3,82	0,82	1,58
6	1,97	0,72	0,38	4,13	1,00	1,38
7	2,00	0,69	0,33	4,14	0,72	1,76

It is found that during the oxidation the relative content of methyl CH_2 and methylene CH_3 groups varies considerably, thus, the chipping of alkyl substituents with the formation of volatile oxidized hydrocarbon derivatives, which are partially removed as a slip stream. Due to this, the total content of the methyl and methylene groups slightly increases the oxidation products. At that the developed fragments of an aromatic ring $\text{C} = \text{C}_{\text{arom}}$, are included in polycondensation reaction to form most of high molecular compounds, asphaltenes. At that oxidized fragments are introduced in the bitumen structure. Apart from a slight increase of paraffin structure share ($\text{CH}_3 + \text{CH}_2$) with respect to aromatic ones the increase of aromatic carbonyl compound $\text{C} = \text{O}$ content is observed. Thus, during the oxidation, the proportion of carbonyl groups is increased with a simultaneous increase of sulfideoxide groups SO . Probably, it is related with the complexity of sulfur compounds conversion in the oxidation process.

The introduction of activating complex at 200 °C changes significantly the structure of an average tar molecule. Alifaticity decreases, indicating the increase in the proportion of aromatic structures. At that, the condensation of aromatic structures increases two times. The reduction of paraffin structure branching and the appearance of the carbonyl groups (table 4 and 5) into tar is related to the presence of organic acids in the composition of an activating complex. The heating of an activating tar at a high temperature of 250 °C during the first hour deepens the marked changes of tar hydrocarbon structure, increases the fraction of ethers and reduces the fraction of acids. The reduction of alifaticity and the increase of tar condensation with an activating complex by heating may be associated with a separation from the aromatic nuclei of aliphatic substituents with their subsequent condensation.

3. Conclusion

During the oxidation the content of carbonyl groups in the acids does not change, and it is reduced slightly in complex ether groups. On the basis of relationship studies concerning the changes of structural-group composition on the oxidation time of tar with a modifying additive one may conclude that the drop of alifaticity occurs mainly due to the methyl and methylene groups of long aliphatic chains as the total content of paraffinic structural elements in the bitumen, remains almost unchanged depending on an oxidation period.

4. Summary

According to the obtained data (Table 5), oxidation process takes place most intensely during the first hour which is evidenced by the sharp decline of alifaticity and condensation increase due to the oxidative cracking reactions accompanied by the cleavage and oxidation of paraffinic and cycloparaffinic substituents in aromatic structures. A considerable growth of obtained products oxidation occurs simultaneously. A further increase of oxidation time does not significantly change these characteristics, which is related probably to the accumulation of aromatic systems of a higher condensation degree, which are formed by the dehydrogenation and polycondensation of structural fragments with atmospheric oxygen. However, it should be noted that the oxidation of tar reduces alifaticity and increases the condensation of oxidation products in a lesser extent than during the preceding activation of tar. The branching of paraffinic chains during oxidation decreases. The fluctuations in the values of branching indicate periodic spending and the accumulation of branched paraffinic structures, are conditioned by the fact that tertiary carbon atoms are more reactive.

5. Conflict of Interest

The author confirms that the presented data do not contain any conflict of interest.

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