



STUDY OF PHYSICO-CHEMICAL CHARACTERISTICS OF THE BITUMEN OBTAINED BY AEROBIC CATALYTIC OXIDATION OF OIL TAR

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ABSTRACT

The article considers the way to improve the quality of bitumen. In order to improve the quality characteristics of bitumen, the authors propose introducing special additive (catalyst-modifier) into the tar during its oxidation. The effect of a manganese-containing catalyst synthesized on the basis of petroleum acids on the rate of obtaining road bitumen from petroleum tar by means of a liquid-phase oxidation process was studied. The conducted studies have established that the introduction of the catalyst in various concentrations (0.1-0.5 wt.%) and a change in the amount of supplied air (0.3-0.6 l/min) leads to an increase in the rate of bitumen production. Based on the obtained experimental data, the optimal amount of catalyst (0.3 wt.%) and air supply rate (0.6 l/min) at the most acceptable oxidation process temperature of 260±2 °C were determined. Analysis of the elemental composition of the initial tar and the obtained bitumen samples showed that the oxidation process significantly increases the amount of oxygen and reduces the amount of hydrogen. In particular, during oxidation in the presence of a catalyst, the amount of oxygen reaches its maximum level, which confirms the effectiveness of the reaction. The results of structural-group analysis show significant changes in the structure of molecules that occur during oxidation: chain rupture, changes in the ratio of saturated and unsaturated fragments, an increase in the number of substitutions in aromatic nuclei. Thus, the oxidation process carried out in the presence of a catalyst has a more effective and profound effect in terms of structural changes.

Keywords: tar; liquid-phase oxidation; manganese-containing catalyst; road bitumen.

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1. Introduction

Bitumen is a typical petroleum-dispersed system formed by high-molecular asphaltene and paraffin associates distributed in a maltene dispersion medium [1]. This may be the reason for the intricate relationship between the structure, composition, and properties of bitumen, including a fairly high sensitivity to changes in parameters during production and operation. Therefore, modeling (regulation) the bitumen production process and forecasting the quality indicators of the resulting product is a complex task in the production process of bitumen [2, 3].

Improving the industrial technology of oxidized bitumen production in order to improve its quality can be implemented by reconstructing the installations, changing the technological parameters of production, introducing additional operations to regulate the quality indicators of bitumen. However, solving the problem in this way is associated with

significant material costs and leads to an increase in the cost of the final product. Therefore, the development of effective and low-cost methods of influencing the macroproperties of the system by changing its microproperties is an urgent task.

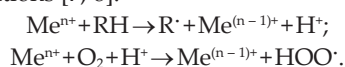
In this regard, various technological methods are currently used to regulate the quality of the bitumen obtained, which are carried out by introducing various modifying additives into the oxidation process. The additives are divided into two main groups [4-6]:

1. the use of additives containing polycyclic aromatic hydrocarbons, which are structurally similar to components of the petroleum system (e.g., petroleum products, resins, resinous-asphaltene substances). This type of additives affects the structure of the components of the oil dispersed system by regulating phase transitions and changing the molecular-dispersed state of the original oil system [7];
2. the use of substances (modifiers) that initiate or catalyze the tar oxidation process. Such catalysts include various salts of metals of variable valence, salts of

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mineral and organic acids or compositions based on them. The introduction of such compounds into the oxidation process allows to reduce the duration of the process. The catalytic action of salts of metals of variable valence is due to the formation of free radicals as a result of their oxidation-reduction transformations [7, 8]:



The production of bituminous materials from heavy petroleum residues involves multi-stage operations, which include not only the oxidation of the residue but also the modification of the feedstock to achieve the required material quality [9]. Although the use of modifiers significantly improves bitumen properties [10], their integration into the production process is labor-intensive, requiring additional

equipment and a separate stage in the process flow [11]. Therefore, the solution to the problem of improving the quality of bitumen is possible by introducing additives at the time of tar oxidation [12]. This will make it possible to: 1) use the additive more economically, because during oxidation, a more complete dissolution of the additive in the product will occur; 2) it will be possible to shorten the production chain by eliminating the stage of compounding with bitumen material. Thus, compared to bitumen obtained from unmodified tar, a higher quality material will be obtained (fig. 1).

The work aims to study the principles of the liquid-phase oxidation of petroleum tar using a modifier-catalyst based on a manganese-containing salt of natural petroleum acids, which affects the structure of the original petroleum product and the quality indicators of the resulting bitumen.

2. Experimental part

As part of the study, tar oxidation processes were carried out both in the presence and absence of a modifier-catalyst in order to compare the properties of the obtained bitumen and to identify the effectiveness of the modifier-catalyst.

As a feedstock, petroleum tar obtained at the Heydar Aliyev Oil Refinery during the primary oil-refining process was used. The physicochemical and quality indicators of the tar are presented in table 1.

A manganese-containing salt of natural petroleum acids (Mn-NPA) synthesized according to the method [13] was investigated as a modifier-catalyst. The oxidation process was carried out in a laboratory bubbling-type unit (fig. 2) at a temperature of 260 ± 2 °C, with an air flow rate of 0.3-0.5-0.6 l/min per 100 grams of petroleum tar. The choice of this temperature for the oxidation process is based on the temperature used in industrial units.

The oxidation procedure is presented below:

- thermal oxidation of tar (in the absence of a modifier-catalyst) in an oxidation column at a temperature of 260 ± 2 °C and an air flow rate of 0.3-0.6 l/min.;
- preparation of raw materials (introduction of Mn-NPA to tar at a concentration of 0.1; 0.3; 0.5% by weight), mixing until homogeneous with tar at a temperature of 150 °C, after thermal oxidation in an oxidation column at a temperature of 260 ± 2 °C and an air flow rate of 0.3-0.6 l/min.;
- determination of quality indicators («ring-and-ball» softening point, penetration at 25 °C, Fraass breaking point, ductility at 25 °C, and adhesion to mineral fillers) of the obtained bitumen according to GOST AZ 3536601.242-2015.

Elemental analysis was performed on a TrusPec Micro analyzer (LECO, USA).

IR spectra and images of their surfaces were recorded on a LUMOS IR Fourier microscope (Bruker, Germany), in the wavenumber range of $4000-600$ cm^{-1} .

NMR ^1H and NMR ^{13}C spectra were recorded at 20 °C on a BRUKER-Fourier spectrometer (300 MHz), using tetramethylsilane as an internal standard and CDCl_3 as a solvent. Structural group analysis of petroleum tar (Sample-1) and the obtained bitumen samples «without» and «with» the addition of a catalyst (Sample-2, Sample-3) was carried out on the basis of NMR ^1H spectra, taking into account elemental analysis, average molecular weight, empirical formula and infrared spectroscopy data.

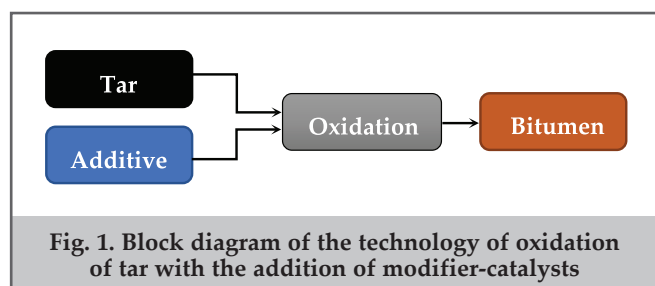


Fig. 1. Block diagram of the technology of oxidation of tar with the addition of modifier-catalysts

Indicator name	Value
Initial bubble point, °C	Not lower 450
Group composition, % wt.:	
asphaltenes	16.6
resins	18.8
oils	64.6
Ring-and-ball softening point, °C	28.5
Open-cup flash point, °C	>286
Coking properties, % wt.	11.48
Sulfur content, % wt.	0.48

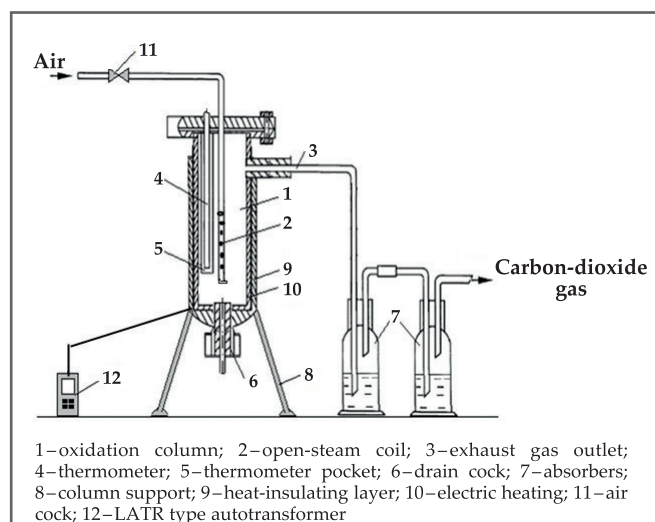


Fig. 2. Laboratory unit for aerobic oxidation of tar to obtain bitumen

Also, the thermal properties of Sample-1, Sample-2 and Sample-3 were studied using thermographic analysis. The studies were conducted on a synchronous thermal analyzer Jupiter STA 449F3 (NETZSCH, Germany) in dynamic mode, in an inert (nitrogen) environment in the temperature range of 25–650 °C, with a temperature increase rate of 10 °C/min.

3. Results and their discussion

Comparative analyses of the quality indicators of bitumen obtained from tar with low quality indicators and bitumen obtained from the same tar sample with the addition of Mn-NPA were performed. Bitumen samples obtained in the presence of 0.1% wt. and 0.5% wt. of Mn-NPA were obtained in a longer period of the oxidation process and with worse quality indicators. With an increase in the catalyst concentration, an inhibitory effect was observed. In order to compare the quality indicators, the physicochemical characteristics of the oxidized bitumens obtained from tar «without» and

«with» the addition of Mn-NPA (0.3% wt.) are presented in tables 2 and 3.

Figure 3 shows graphical dependences of the softening temperature of bitumen obtained «without» and «with» adding a catalyst on the oxidation time.

Analysis of the data in the tables and the presented graphs demonstrates that the introduction of Mn-NPA additive in the amount of 0.3% by weight per 100 grams of the feedstock leads to an acceleration of the oxidation process of petroleum tar and allows to reduce the oxidation time when obtaining oxidized bitumen with the required quality indicators according to GOST. At the same time, the oxidation conditions contribute to the transformation of petroleum tar components into compounds that have a positive effect on the performance properties of the bitumen material – such as plasticity, stability, and adhesion.

The results of the elemental analysis of the samples are presented in figure 4.

Table 2

Physicochemical characteristics of oxidized bitumens obtained by oxidation of tar without adding a modifier-catalyst

Indicator name	The norm for BND 50/70	Air flow rate, l/min		
		0.3	0.5	0.6
Oxidation time, h	-	25	25	15
Softening point according to GOST, °C	46-54	38.5	46	46
Fraass breaking point, °C	≤-15	-	-25	-23
Ductility at 25 °C, mm	≥55	-	87	>100
Penetration at 25 °C according to GOST	51-70	-	54	56
Adhesion, mark	1, 2, 3	-	3	2

Table 3

Physicochemical characteristics of oxidized bitumen obtained by oxidation of tar with the addition of a modifier-catalyst (concentration – 0.3% wt.)

Indicator name	The norm for BND 50/70	Air flow rate, l/min		
		0.3	0.5	0.6
Oxidation time, h	-	19	17	9
Softening point according to GOST, °C	46-54	38.4	47.8	48
Fraass breaking point, °C	≤-15	-	-22	-21
Ductility at 25 °C, mm	≥55	-	68	>100
Penetration at 25 °C according to GOST	51-70	-	53	54
Adhesion, mark	1, 2, 3	-	2	1

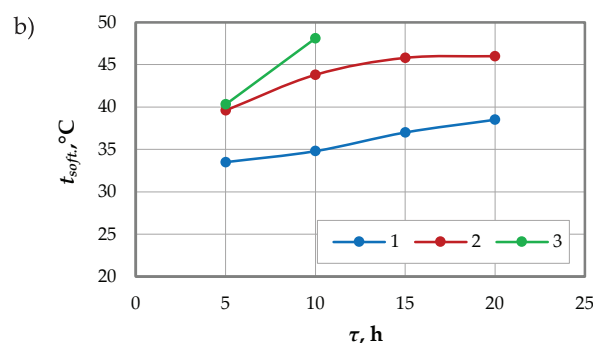
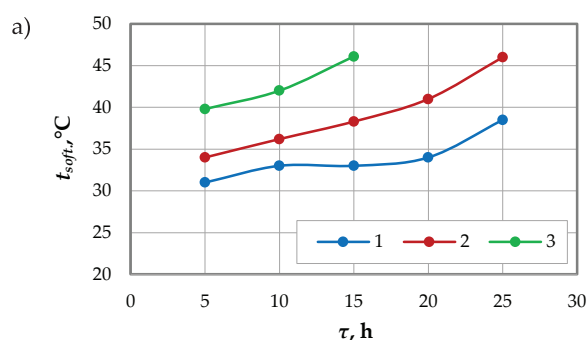


Fig. 3. Dependence of softening temperature on the time of the tar oxidation process «without» (a) and «with» (b) adding a catalyst (0.3 wt. %): 1–0.3 l/min., 2–0.5 l/min., 3–0.6 l/min

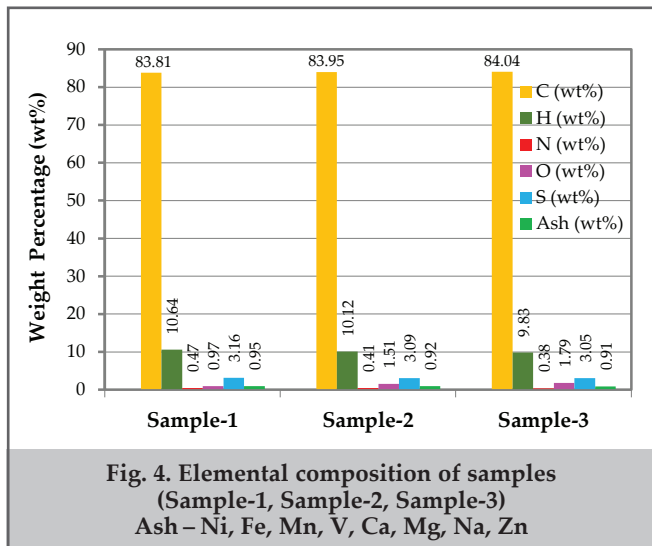


Table 4

Density, average molecular weight and average empirical formula of samples

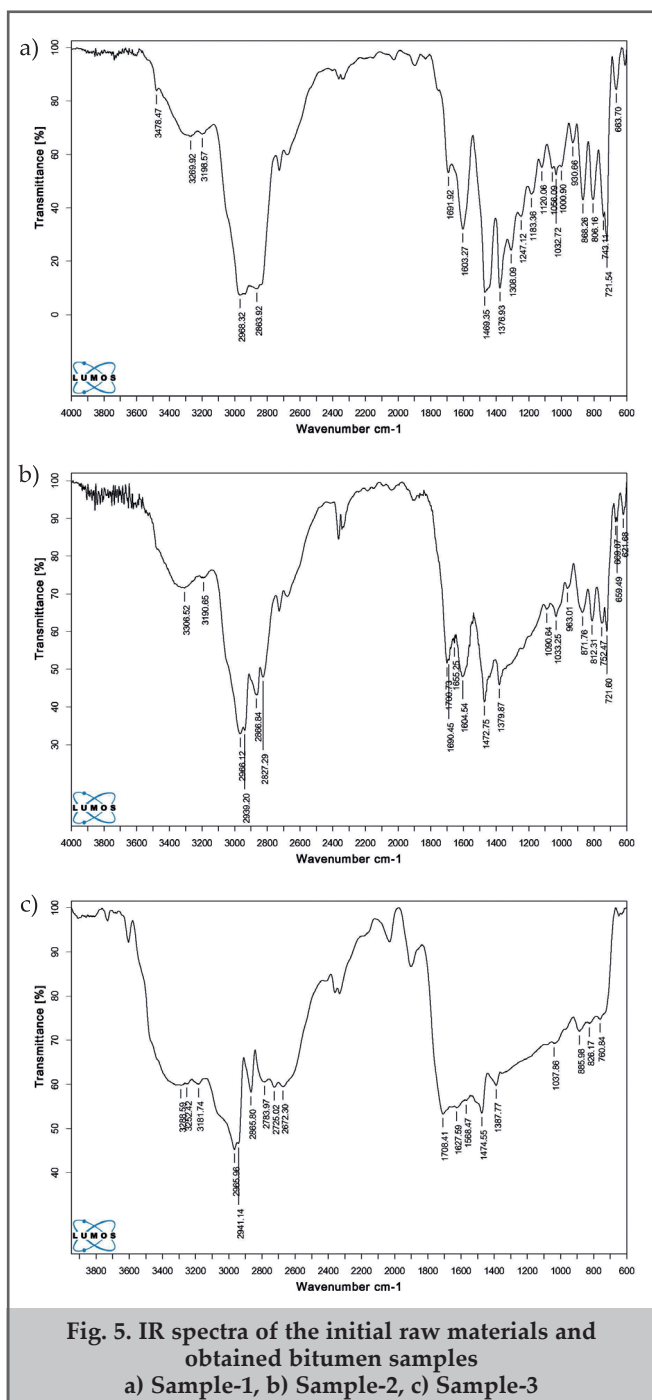
Samples	²⁰ d ₄ (g/sm ³)	¹⁵ d ₁₅ (g/sm ³)	MW	Empirical formula
Sample-1	0.9655	0.9687	706.71	C _{49.4} H _{75.2} N _{0.24} O _{0.43} S _{0.70}
Sample-2	0.9767	0.9796	860.84	C _{60.2} H _{87.1} N _{0.25} O _{0.81} S _{0.83}
Sample-3	0.9847	0.9836	933.33	C _{65.4} H _{91.7} N _{0.25} O _{1.04} S _{0.89}

As can be seen from figure 4, although the amount of carbon increased slightly as a result of the oxidation process, a decrease in the amount of hydrogen was observed (Sample-1 – 10.64%, Sample-2 – 10.12%, Sample-3 – 9.83%). This can be explained by an increase in the amount of aromatic fragments. However, the observed increase in the mass fraction of oxygen (Sample-1 0.97% → Sample-2 1.51% → Sample-3 1.79%) confirms that the oxidation reactions were successful. A more significant increase in the amount of oxygen during oxidation, especially in the presence of a catalyst, indicates a greater efficiency of this process. A slight decrease was recorded in the amount of nitrogen and sulfur, which may be associated, in particular, with an increase in the oxygen content. The amount of other elements (ash-forming materials) in all samples remained almost constant. Overall, the results show that the oxidation processes performed affected the chemical composition of the samples, but the presence of the catalyst made this process more effective, especially in terms of increasing the oxygen and carbon content and decreasing the hydrogen content. The densities, average molecular weights and average empirical formulas of the samples (Sample-1, Sample-2, Sample-3) were calculated and are given in table 4.

It is evident from table 4 that the density and average molecular weight of the sample increased after oxidation. This can be explained by the fact that oxygen penetrates into the molecules, and the molecule grows further as a result of the rearrangement. It should be noted that a greater increase in the density and average molecular weight is observed in Sample-3, obtained as a result of oxidation in the presence of a catalyst. If we look at the empirical formulas, an increase is observed in all atoms. The main change was recorded in the number of C, H and O atoms, and the number of oxygen atoms in Sample 3 increased more than 2 times. The above indicates that the oxidation process occurs more efficiently in the presence of a catalyst.

On the surface images of all samples, 5 points were selected, their IR spectra were taken (fig. 5) and the corresponding 3D images of the models were shown in figure 6.

Analysis of the IR spectra of Sample 1 (point 1) showed that there are absorption bands at 1376, 1469 and 2863, 2968 cm⁻¹, characteristic of deformation and stretching vibrations of the C-H bond of the CH₃ and CH₂ groups; 693, 721, 743, 806, 868 cm⁻¹ – deformation vibrations of the C-H bond of the benzene ring; 1603 cm⁻¹ – stretching vibrations of the C-C bond of the benzene ring; 3198, 3269, 3478 cm⁻¹ – stretching vibrations of the N-H bond; 1691 cm⁻¹ – characteristic of the C=O bond. Comparing points 1 and 2, 3, 4, 5 of Sample-1, we can conclude that they are identical. The analysis of IR spectra of Sample-1 (point 1) with Sample-2 (point 1) showed that along with the previously listed absorption bands on the spectrum of point 1 of Sample-2 there are absorption bands

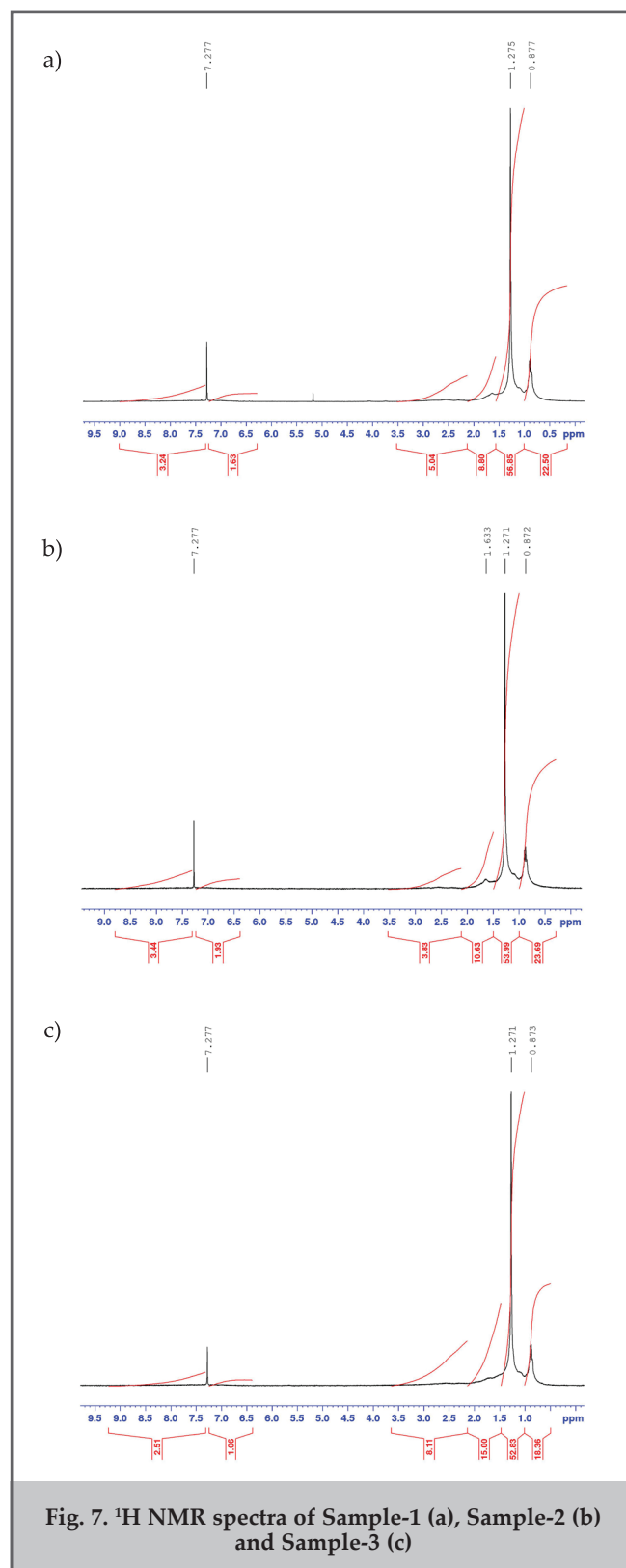
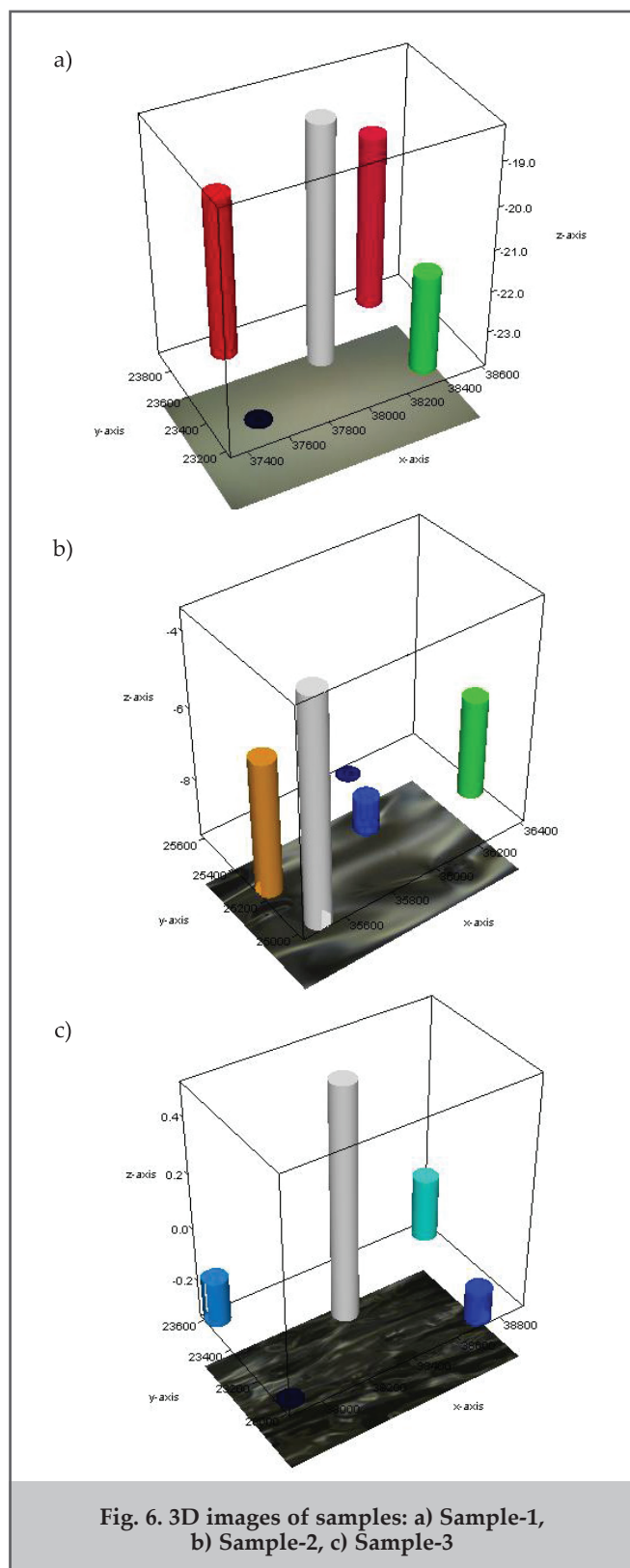


at 1700 cm^{-1} , characteristic of the stretching vibrations of the C=O bond, at 1655 cm^{-1} – the C=O bond of the amide. An identical picture is also observed for Sample-3. Thus, the IR spectroscopy method showed that the spectra of Sample-2 and Sample-3 show the formation of different C=O groups.

The images of NMR spectra of Samples-1, 2, 3 are presented below in figure 7.

It is evident from the spectra of the samples that the resonance signals are practically indistinguishable due to the chemical shift zones (fig. 7). Thus, the resonance signal

recorded in the range of 0.65–1.00 ppm in all three spectra refers to the terminal methyl group (H_γ), the signal observed in the range of 1.00–1.50 ppm refers to the CH_2 groups and some CH groups included in the alkyl chain (H_β), and the signal in the range of 1.50–2.10 ppm – to the naphthene rings (H_α). Also in the spectra, the CH_2 and CH groups located in the α -position relative to the aromatic rings (H_α) were recorded in the range of 2.10–3.50 ppm, and the protons belonging to the aromatic nucleus (H_{Ar}) were recorded in the range of 6.50–8.70 ppm [15–17].



In the ^{13}C NMR spectrum of Sample-1, the carbon atoms belonging to methyl groups were observed at 14.15, 18.45 ppm, CH_2 groups at 19.76, 22.72 ppm, carbon atoms belonging to saturated rings at 29.39, 29.73 ppm, carbon atoms attached to the aromatic nucleus at α -position at 31.95 ppm, and aromatic carbon atoms at 127.50 and 128.14 ppm. The signals in the ^{13}C NMR spectrum of Sample-2 are close to the spectrum of Sample-1. The most striking point is that no signal is observed at 19.76 ppm. This also indicates that the change of CH_2 groups of the chain occurs. The main change is observed in the spectrum of Sample-3, as an additional signal is recorded at 29.62 ppm. This reflects an increase in the number of carbon atoms belonging to the naphthenic fragment. In addition, the shift of the signals belonging to the aromatic ring towards the weak region and the observation of an additional signal (127.48 ppm) indicate that the substitution occurred in the aromatic ring. The key point in the ^{13}C NMR spectrum of Sample-3 is the registration of a signal at 170.56 ppm. This signal belongs to the carboxyl group of carbon ($\text{C}=\text{O}$) and indicates that the oxidation process proceeds more successfully in the presence of a catalyst.

In the structural group analysis, according to literary data [14-20], saturated and unsaturated fragments, the number of carbon and hydrogen atoms in these fragments, the number of saturated and unsaturated rings, the lack of protons in the molecule, the degree of substitution in aromatic nuclei, etc. are calculated.

The relative distribution of hydrogen atoms in the spectra by structural groups (in %) was calculated based on literary sources [14, 15, 17, 18] and is given in table 5.

In the table 5, the different values of hydrogen atoms belonging to the same fragments provide important insights into the oxidation process. Thus, the increase in the J (0.29) and H_γ (24.29%) values in Sample-2 indicates the cleavage of the alkyl chain and the formation of branched alkyl fragments. Also, the decrease in the H_p value (55.37%) once again proves the shortening of the chain. It is observed that the H_n value in Sample 2 increases to about 2%. This indicates that some of the radicals formed as a result of chain cleavage form naphthenic fragments. On the other hand, the decrease in the H_α value reflects the fact that the chain is also cleaved at the point where it attaches to the aromatic ring. This situation is also observed with the increase in the H_{Ar} value. It is noted that in Sample-3, the processes proceed relatively differently. Thus, although we infer chain scission and shortening from the decrease in H_p value (53.97%), the significant decrease in J (0.23) and H_γ (18.76) values indicates that chain branching has hardly occurred. Compared with Sample-1, the amount of hydrogen (H_n) belonging to naphthenic rings in Sample-3 has increased by more than 6%. Therefore, a certain part of the radicals generated by

chain scission forms naphthenic fragments. Another striking point is the significant increase in H_α value in Sample-3 (8.29%) compared to Sample-1. This means alkylation of the aromatic ring. In addition, the decrease in H_{Ar} and f_a values increases the probability of replacing aromatic hydrogens with alkyl fragments. Thus, oxidation with and without catalyst is accompanied by different structural changes. For a more visual explanation of the tar oxidation process, the average numbers of hydrogen atoms, carbon, saturated and unsaturated rings in the samples, the hydrogen deficiency in the molecule and the degree of substitution in the aromatic rings were calculated and are given in table 6.

Table 6 shows the changes in the structural group parameters for Sample-1, Sample-2, and Sample-3. These changes help to reflect how the oxidation reactions proceed at the molecular level. Table 6 agrees with table 5 in many respects. However, there are some notable points. Thus, in the oxidation process, along with the rearrangement, it is also necessary to take into account the molecular growth. If we pay attention to the number of methyl groups in the table (H_γ and C_γ), we will see a significant increase in Sample-2 ($H_\gamma=21.2$ and $C_\gamma=7.1$). This indicates that the number of methyl groups in Sample-2 increased as a result of the branching of the long chain. In Sample-3, the number of methyl groups decreased ($C_\gamma=5.8$), the broken radicals formed naphthenic fragments ($H_n=14.1$) and replaced aromatic hydrocarbons ($H_\alpha=7.6$). For this reason, a decrease in the amount of aromatic hydrocarbons ($H_{Ar}=3.3$) is observed in Sample-3. In fact, the decrease in aromatic hydrocarbons in Sample-3 does not mean a decrease in the amount of aromatic hydrocarbons, but rather alkylation of the aromatic ring. The main parameter that does not correspond to table 5 is the hydrogen atoms (H_p) of the paraffin fragment. Thus, although table 6 shows an increase in the number of hydrogen atoms belonging to the chain from Sample-1 to Sample-3 (Sample-1 – 43.7 → Sample-2 – 48.2 → Sample-3 – 49.5), table 5 shows a decrease in the percentage of this parameter. This happens because the molecule grows as a result of oxidation. That is, if we take into account the growth of the molecule, it would be wrong to say that the chain is lengthened. A significant increase (7.9 → 11.4 → 16.3) is recorded in the total number of rings (R_t). Therefore, the radicals formed during chain rupture were mainly used to form saturated rings (R_s) (5.7 → 8.5 → 14.4). Interestingly, in sample-3, a decrease in the number of aromatic rings (R_{Ar}) is observed. However, it is difficult to come to such a conclusion using only the ^1H NMR experiment. As mentioned above, it is necessary to take into account the alkylation of aromatic nuclei and, therefore, the reduction of aromatic hydrogens. For the initial clarification of this issue, the parameters of hydrogen deficiency (Z) in the molecule and the degree of substitution (σ) in aromatic rings were calculated. As can be

Table 5
Relative distribution of hydrogen atoms by structural groups (H_γ , H_p , H_n , H_α , H_{Ar}) in samples.
Isoparaffin index and degree of aromaticity

Sample	Relative distribution of hydrogen (%)					Isoparaffin index J	Degree of aromaticity f_a
	H_{Ar}	H_α	H_n	H_p	H_γ		
Sample-1	4.95	5.12	8.92	58.05	22.96	0.26	0.20
Sample-2	5.51	3.93	10.90	55.37	24.29	0.29	0.21
Sample-3	3.65	8.29	15.33	53.97	18.76	0.23	0.13

Table 6

Structural-group parameters of Sample-1, Sample-2 and Sample-3														
Sample-1					Sample-2					Sample-3				
The number of hydrogen atoms					The number of hydrogen atoms					The number of hydrogen atoms				
H _{Ar}	H _α	H _n	H _p	H _γ	H _{Ar}	H _α	H _n	H _p	H _γ	H _{Ar}	H _α	H _n	H _p	H _γ
3.7	3.8	6.7	43.7	17.3	4.8	3.4	9.5	48.2	21.2	3.3	7.6	14.1	49.5	17.2
The number of carbon atoms					The number of carbon atoms					The number of carbon atoms				
C _{Ar}	C _α	C _n	C _p	C _γ	C _{Ar}	C _α	C _n	C _p	C _γ	C _{Ar}	C _α	C _n	C _p	C _γ
9.9	2.3	8.1	23.3	5.8	12.6	2.2	9.3	29	7.1	8.5	4.8	10.6	35.7	5.8
The number of rings			The number of rings			The number of rings								
R _t	R _{Ar}	R _s	R _t	R _{Ar}	R _s	R _t	R _{Ar}	R _s						
7.9	2.2	5.7	11.4	2.9	8.5	16.3	1.9	14.4						
Proton deficiency		Degree of substitution in Ar		Proton deficiency		Degree of substitution in Ar		Proton deficiency		Degree of substitution in Ar				
Z	Σ	Z	σ	Z	σ									
23.6	0.38	33.3	0.31	39.1	0.59									

Note: H_γ – average number of hydrogen atoms belonging to terminal methyl groups; H_p – average number of hydrogen atoms belonging to the paraffin chain; H_n – average number of hydrogen atoms belonging to the naphthene fragment; H_α – average number of hydrogen atoms attached to the aromatic ring in the α position; H_{Ar} – average number of hydrogen atoms belonging to the aromatic nucleus; C_γ – average number of carbon atoms belonging to the terminal methyl groups; C_p – average number of carbon atoms belonging to the paraffin chain; C_n – average number of carbon atoms belonging to saturated rings; C_α – average number of carbon atoms bonded to the aromatic ring in the α position; C_{Ar} – average number of carbon atoms belonging to the aromatic nucleus; R_t – average total number of rings; R_{Ar} – average number of aromatic rings; R_s – average number of saturated rings; Z – proton deficiency in the molecule; σ – degree of substitution in the aromatic nucleus

seen from table 6, a significant increase in both indicators is observed in Sample-3 (Z – Sample-1 – 23.6 → Sample-2 – 33.3 → Sample-3 – 39.1, σ – Sample-1 – 0.38 → Sample-2 – 0.31 → Sample-3 – 0.59). Taking into account the above, it can be noted that the number of aliphatic substituted aromatic fragments increased in Sample-3.

The thermal stability of Samples-1, 2, 3 was studied under optimal conditions and the obtained thermogravimetric curves are presented below (fig. 8).

In the temperature range of 300–400 °C, the mass loss in Sample-1, taken as the starting material, is 7.08%, in Sample-2 – 9.85%, and in Sample-3 – 5.57%. Despite the fact that the maximum destruction in all samples is almost the same, the main destruction process in Sample-1 is in the range of 313.1–498.9 °C and decomposition occurs in several stages: at 313.1 °C – the first decomposition, due to the rupture of covalent bonds; in the range of 444.7–498.9 °C – the second decomposition. In Sample-2, destruction is in the range of 412.5–504.3 °C, but also occurs in several stages, and the total mass loss is 65.48%. The main decomposition process in Sample-3 occurs in the temperature range of 427.8–520 °C in one stage. Due to the influence of Mn-PNA used as a catalyst, the destruction of bitumen obtained from tar is less in the temperature range of every 100 °C up to 427.8 °C.

In the entire temperature range under study, the thermal stability of bitumen obtained in the presence of a catalyst is significantly higher than of the original tar, which is expressed in a lower mass loss. Particularly noteworthy is the fact that the thermal stability of bitumen obtained by non-catalytic oxidation of tar is significantly lower than of the original tar and bitumen obtained by oxidation in the presence of a catalyst. This bitumen begins to undergo transformations already at a temperature of about 100 °C and in the entire temperature range under study is characterized by high mass loss values.

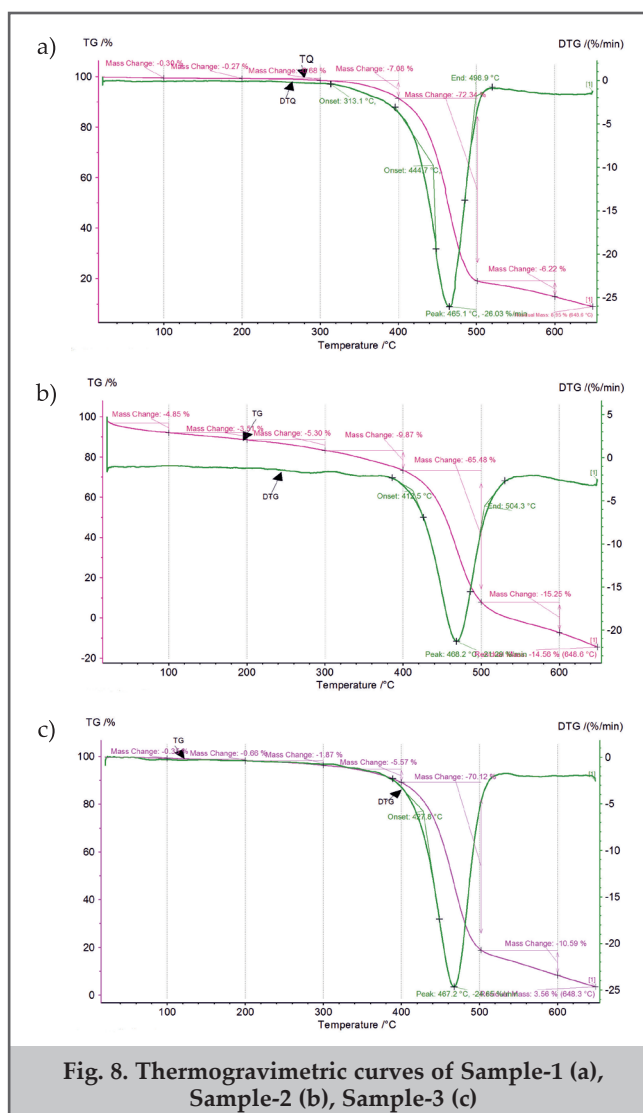


Fig. 8. Thermogravimetric curves of Sample-1 (a), Sample-2 (b), Sample-3 (c)

Conclusions

1. The introduction of a catalyst modifier into petroleum tar, which affects the structure of the petroleum system, changes the rate of the oxidation process. It was found that Mn-NPA has a catalytic effect on the process at an optimal content of Mn-NPA in the tar (0.3 wt.%) and an air flow rate of 0.6 l/min.
2. The oxidation process significantly affected the chemical composition and structure of the tar sample. In particular, oxidation carried out in the presence of a catalyst (Sample-3) was accompanied by more effective changes:
 - according to the results of elemental analysis, the amount of oxygen as a result of oxidation increased from 0.97% in Sample-1 to 1.79% in Sample-3. The amount of hydrogen, on the other hand, decreased from 10.64% (Sample-1) to 9.83% (Sample-3). This phenomenon is associated with an increase in the number of aromatic fragments and chain rupture;
 - the average molecular weight was 706.71 g/mol for Sample-1, 860.84 g/mol for Sample-2 and 933.33 g/mol for Sample-3. This increase was due to the incorporation of oxygen into the molecule and rearrangement;
 - in the structural group analysis, the number of hydrogen atoms belonging to naphthenic fragments (H_n) in Sample-3 increased significantly: from 6.7 → 9.5 → 14.1. This indicates chain rupture and formation of naphthenic structures as a result of oxidation.
3. The obtained thermogravimetric curves confirm that Sample-3 is thermally more stable and durable, in comparison with Samples-1 and Sample-2.

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