

PRODUCTION OF BITUMEN MODIFIED WITH LOW-MOLECULAR ORGANIC COMPOUNDS FROM PETROLEUM RESIDUES. 7. STUDY OF THE STRUCTURE OF FORMALDEHYDE MODIFIED TARS

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Abstract. Three samples of bituminous material with different softening temperatures of 321, 332, and 356.4 K were obtained by the method of chemical modification of tar with formaldehyde using sulfuric acid as a catalyst. The determination of the group hydrocarbon composition was carried out for the raw materials of the modification process (tar) and the resulting bitumens. An FTIR study of the obtained groups of hydrocarbons (oil, resins, and asphaltenes) was also carried out. The structural transformations were investigated and a possible chemistry of the tar modification process with formaldehyde was proposed.

Keywords: tar, bitumen, formaldehyde, chemical modification.

1. Introduction

As is nowadays known, the main reaction occurring as a result of the chemical interaction of aromatic hydrocarbons of petroleum residues and formaldehyde is the reaction of arene-formaldehyde condensation.^{1,2} Historically, the earliest studies related to the study of mechanism and the study of the influence of the factors of this process began as early as the 19th century. However, there is still a need to intensify the process and study the structure of the products synthesized *via* the chemical interaction between arenes and formaldehyde.

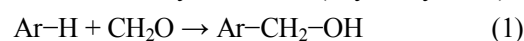
Thus, synthesis in the area of arene-formaldehyde condensations began with the experiments of T. Zinke,^{3,4} resulting in the formation of diphenylmethane through condensation of benzyl chloride with benzene. His suc-

cessor, and later a pioneer, was A. Bayer, who by changing the reaction conditions, in particular through the use of concentrated sulfuric and later acetic acid, discovered reactions that became the basis for further syntheses by V. Meyer and Wurster.⁵ The reaction of the diphenylmethane formation through the interaction between benzene and formaldehyde (formalin) was first carried out by A.M. Nastyukov in 1903, resulting in the formation of an amorphous non-melting product, phenylformol. Further works of A.M. Nastyukov, as well as the research of A. Bayer laid the foundation for numerous studies in the field of arene-formaldehyde polycondensations, which gave an impetus to the production of various types of resins, which are still widely used.⁶⁻¹⁰ At the Department of Chemical Technology of Oil and Gas Processing of the Lviv Polytechnic National University, research is being conducted related to the production of arene¹¹⁻²³ and phenol-formaldehyde²⁴⁻³¹ resins with the aim of obtaining bituminous materials with improved operational properties.

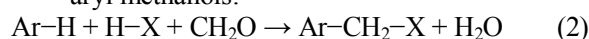
Based on the conducted research, as well as taking into account the experience of the above-mentioned authors, it can be stated that all reactions of aromatic hydrocarbons with either formaldehyde or compounds that can act as formaldehyde donors (methylene diacetate, *etc.*) proceed in the presence of catalysts, such as strong mineral acids, aluminum chloride, zinc chloride, and other Lewis acids.

According to the nature of the products formed, all reactions of formaldehyde with arenes can be divided into the following main groups:

1. Formation of arylmethanols (oxymethylation):



2. Halomethylation and formation of the esters of aryl methanols:



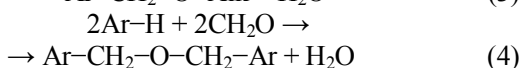
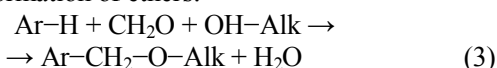
where X is halide or acyl, for example, acetyl.

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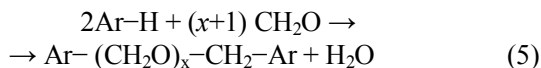
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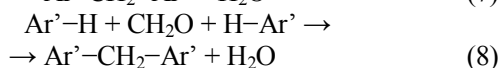
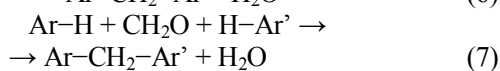
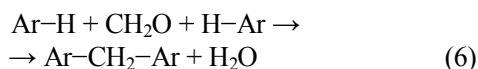
3. Formation of ethers:



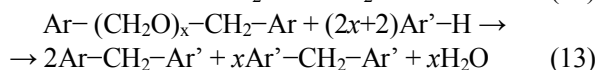
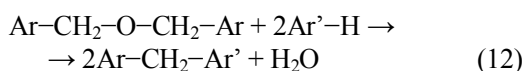
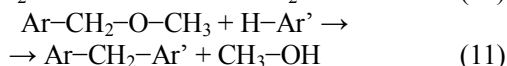
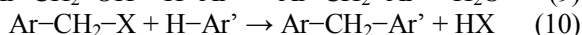
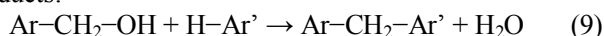
4. Formation of acetals:



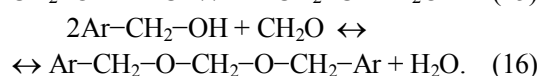
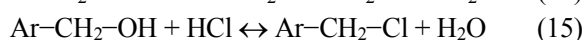
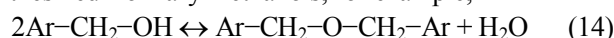
5. Formation of symmetric or asymmetric diaryl-methanes:



Diarylmethanes can be prepared from the reaction products:

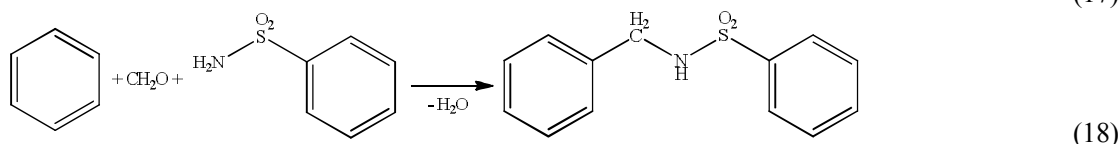
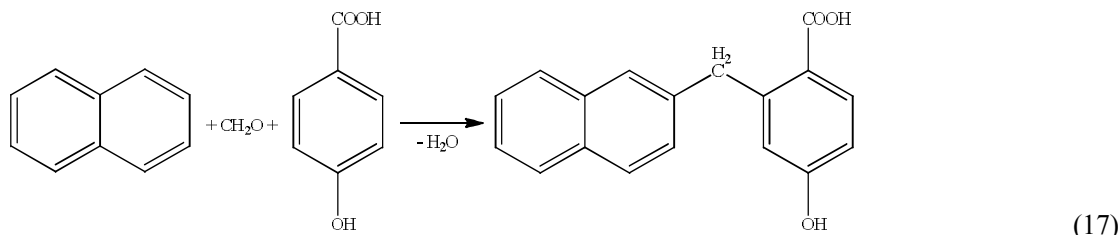


In addition, all reaction products (2-4) can also be synthesized from arylmethanols, for example,



This determined the special role of arylmethanols; A. Bayer, R. Wegler, and other researchers considered them to be intermediate products of all condensation reactions of arenes and formaldehyde.

6. In addition to the above, other reactions similar to (3) and (7) are also possible, in which formaldehyde simultaneously reacts with an aromatic hydrocarbon and its derivative, for example, phenol, carboxylic acid or another compound capable of reacting with it, *e.g.*, with sulfamide:



7. Also, besides one hydrogen atom, two or more hydrogen atoms of an aromatic compound can react with formaldehyde. At the same time, depending on the spatial arrangement of these atoms, cyclic compounds or polymers can be formed in which the connecting moieties between the aromatic rings are methylene, acetal, or ether groups.

Meanwhile, analyzing the above, it is worth noting that the synthesis of arylmethanols according to reaction (1) is complicated by the fact that, in an acidic environment, they quickly undergo further transformations. In this regard, while studying the chemistry of formaldehyde reactions with hydrocarbons, the authors³² paid the main attention to the mechanism of joining of formaldehyde to the hydrocarbon shown in Fig. 1, whereas further reactions (9-12) were considered to be exchange reactions.

The concentration of an acid, which is the process catalyst, is an equally important factor that determines the properties of the formed modified product. This parameter

can vary from 30 % to 70 % and even higher. In turn, an increase in the concentration of sulfuric acid leads to a decrease in the oxygen content in the formed resins and to the accumulation of methylene groups in them. Thus, at an acid concentration of 60 %, oxygen-containing groups are practically absent in the formed resins. On the other hand, a significant increase in acid concentration leads to data distortion due to the sulfonation reaction, while the disadvantage of low concentrations of the catalyst is a decrease in the reaction rate of arene-formaldehyde condensation.³²

Given the wide range of factors that can significantly affect the final characteristics of the product, the purpose of this work was to study the transformations that occur, primarily, with the structural group composition of the binder during chemical interaction with formaldehyde. While the simulation of various conditions of conducting the experiment allowed establishing the most optimal conditions for obtaining a commercial product with the required characteristics.

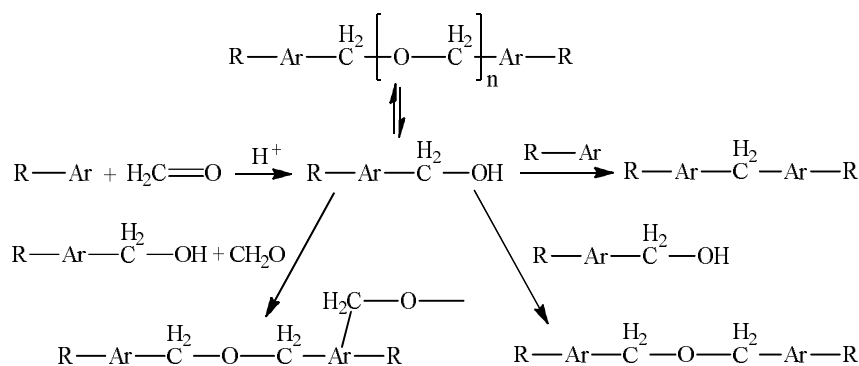


Fig. 1. Chemistry of aromatic compounds co-polycondensation with formaldehyde

Table 1. Physical and mechanical properties of T1

Index	Unit of measurement	Value	Method
Density at 293 K	kg/m ³	982.9	EN 15326 ³³
Initial boiling point	K	659	–
Flash point	K	555	EN ISO 2592 ³⁴
Penetration at 298 K	dmm	247	EN 1426:2015 ³⁵
Softening point (SP)	K	312	EN 1427:2015 ³⁶
Ductility at 298 K	cm	58.1	According to ²⁴
Fraass breaking point (FBP)	K	255	EN 12593 ³⁷
Plasticity interval (PI)	K	57	PI = SP – FBP
Penetration index	–	0.16	EN 12591 ³⁸
Resistance to hardening at 436 K (RTFOT method):			
mass change	wt. %	0.35	EN 12607-1 ³⁹
softening point after RTFOT	K	318.6	
penetration at 298 K after RTFOT	dmm	364	
softening point change	K	6.6	
retained penetration	%	36.8	
Adhesion to gravel	mark	2.5	DSTU 8787 ⁴⁰

2. Experimental

2.1. Materials

Tar (T1) from PJSC Ukratnafta (Ukraine) was used as a raw material for the modification process. Physical and mechanical properties of T1 are given in Table 1.

Formalin, a 37% aqueous formaldehyde solution, was used for chemical modification of tar and bitumen. Concentrated sulfuric acid (density 1.83 g/cm³) was used as a catalyst for the modification process.

2.2. Preparation of modified binders

The products obtained after modification have qualitative characteristics allowing us to classify them as

commercial bituminous road materials that meet the requirements of the standards.

Chemical modification with formaldehyde without stirring was performed in hermetic containers capable of operating under high pressure (Fig. 2) to avoid evaporation of the modifier at operating temperatures (333–433 K). At the loading stage, the temperature in the container must be lower than the boiling point of the modifier.

The scheme of the stages of work on the modification of tar and bitumen with formaldehyde is presented in Fig. 2. The container is loaded with the raw materials (tar or bitumen) and heated to a temperature that ensures that it is fluid. After that, the raw material is allowed to be cooled to a temperature below the boiling point of formalin. Next, a pre-prepared mixture is added: a chemical reagent (formalin) and a catalyst in the required ratio. The

container is sealed, placed in an oil bath at the required temperature and the start time is recorded. After completion of the modification process, the depressurized container is placed in a vacuum cabinet to remove water and the unreacted components. Vacuum drying is performed at 393 K for 4 h.

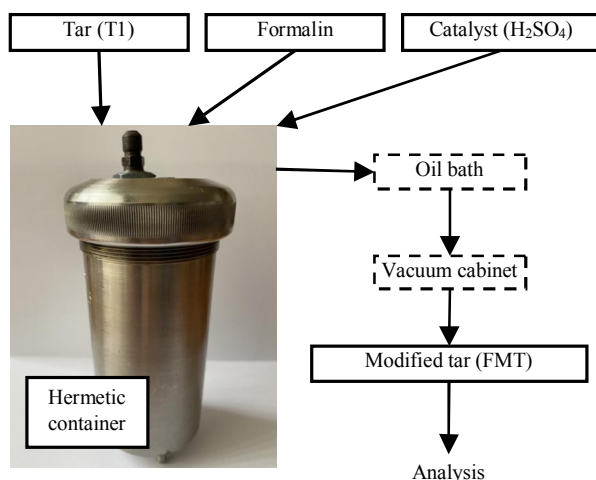


Fig. 2. Scheme of the stages of work on the modification of tar with formaldehyde

2.3. Test methods

The group's chemical composition was determined according to the Markusson method.⁴¹ A weighted portion of bitumen (5 g) was dissolved in 150–200 mL of petroleum ether. To precipitate asphaltenes, a flask with a solution of bitumen (tar) in petroleum ether was placed in a water bath. A reflux condenser was attached to the flask, and the solution was heated to 323 K and kept at this temperature for 30 min. Then, the solution was cooled for 1 h. During this time, asphaltenes, which are insoluble in petroleum ether, precipitated. The sediment also contained carbenes, carboids whereas the petroleum ether solution contained maltenes (oils and resins). Then the formed suspension was filtered. To remove resins and oils, which settled in a small amount together with asphaltenes on the filter, the filter was washed with petroleum ether until the solvent flows out colorless. The sediment obtained on the filter was used to determine the content of asphaltenes, carbenes, and carboids. The filtrate was used to determine the content of resins and oil.

The filter with sediment was placed in a Soxhlet apparatus. 200 mL of benzene was poured into a weighed round-bottomed flask and the Soxhlet apparatus was assembled. Then asphaltenes were extracted at a rate of 2–4 drops per second until all asphaltenes were dissolved (benzene in the extractor should be colorless). The heating was stopped and the flask was cooled. When the solvent (benzene) was distilled out, the mass of asphaltenes was determined.

Compounds insoluble in benzene remained on the filter – carbenes and carboids. After drying the filter, the mass of carbenes and carboids was determined.

100 cm³ of dried silica gel was added to the solution of resins and oil in petroleum ether and mixed. Silica gel adsorbed resins and oils. Silica gel was transferred to a sleeve made of filter paper, which was placed in a Soxhlet extractor. Into a weighed flask, 200 mL of petroleum ether was poured. Then, the Soxhlet device was assembled and the flask was heated. The oils were extracted until there is no pure solvent in the extractor. After this, the heating of the flasks was stopped. The flask was cooled to a temperature below 303 K. After distilling out the solvent (petroleum ether), the weight of the oils was determined.

Resins remained adsorbed on silica gel, desorption of which was done using an alcohol-benzene mixture (1:1). 200 mL of an alcohol-benzene mixture was placed in a weighed flask. The Soxhlet apparatus was assembled. The flask was heated to a temperature of 353–358 K. The intensity of heating should ensure the rate of flow of drops from the ball condenser into the extractor of 2–4 drops per second. After the end of the resin extraction process (the solvent in the extractor had to be colorless), the solution was cooled to 303 K. After distilling out the solvent (alcohol-benzene mixture), the mass of resins was determined.

FTIR spectra were recorded on a Spectrum Two spectrometer (PerkinElmer, USA) using a diamond U-ATR single reflection accessory. PerkinElmer Spectrum software was used to draw the spectra. The spectra (16 scans per spectrum) of the samples were collected in the mid-infrared wavenumber range from 1800 to 400 cm⁻¹, with a spectral resolution of 4 cm⁻¹.

The physical and mechanical properties of bituminous material and methods of their implementation are given in Table 1.

3. Results and Discussion

To study the structure of FMT, in order to produce binding materials for road construction, three samples of FMT with different softening temperatures (321, 332 and, 356.4 K) were obtained. The conditions for obtaining FMT are presented in Table 2. The main physical and mechanical properties of T1 and FMT are shown in Fig. 3.

Fig. 3 shows that, with an increase in the amount of the modifier (formaldehyde), the product viscosity increases, as evidenced by both a decrease in penetration at 298 K (from 247 to 47 dmm) and an increase in the softening temperature (from 312 to 356.4 K). With a significant increase in the softening temperature, the brittleness temperature does not increase significantly (from 255 to 264 K). That is, the obtained bituminous material has a

wide range of plasticity (T1 – 57 K; FMT – 65–92.4 K). Taking into account the above-mentioned research results, it can be concluded that this modification process occurs as a result of the chemical interaction between tar compo-

nents and formaldehyde, *i.e.*, a change in the group composition of the raw materials (T1) proceeds. To confirm this, a group analysis of T1 and FMT was conducted (Table 3 and Fig. 4).

Table 2. Conditions for obtaining FMT

Process parameter	FMT1	FMT2	FMT3
Raw	T1		
Formalin amount (including formaldehyde) (kg/100kg raw)	1.0 (0.37)	1.9 (0.703)	3.0 (1.11)
Catalyst	H ₂ SO ₄		
Catalyst amount (kg/100kg raw)	1.1	1.7	3.2
MRFC	0.91	1.12	0.94
Temperature (K)	383	378	383
Duration (hours)	0.6	0.6	0.8

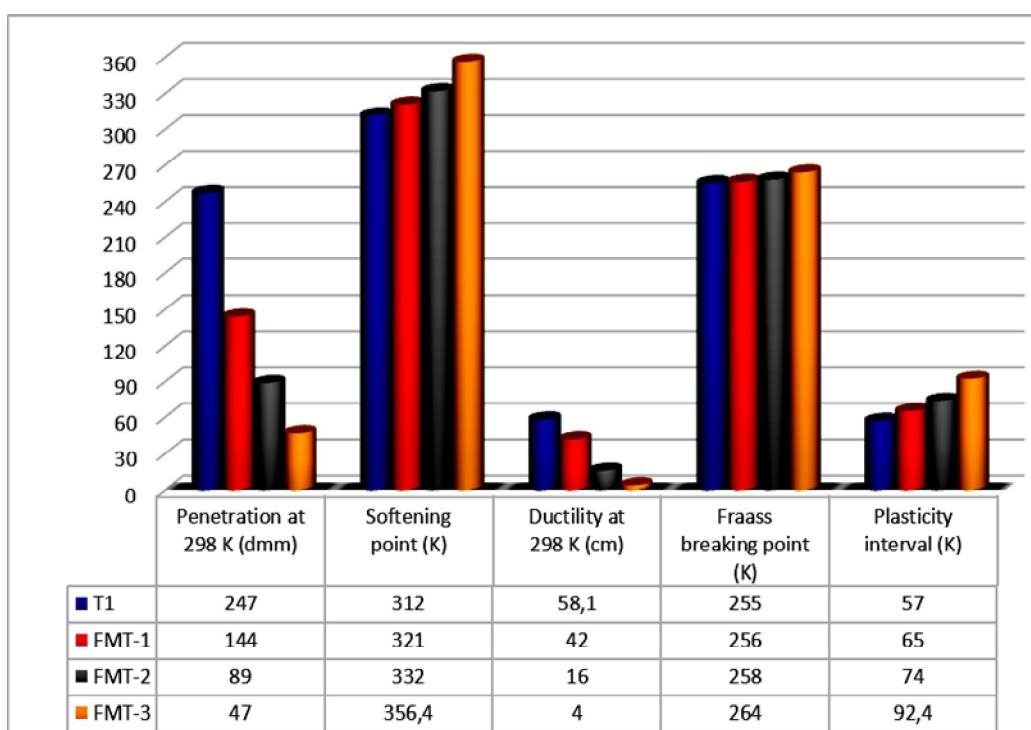


Fig. 3. Physical and mechanical properties of T1 and FMT

Table 3. Group analysis of T1 and FMT

Tar		Content of components in tar				Losses	Total content
		Carbenes and carboids	Oils	Resins	Asphaltenes		
T1	weight (g)	0.01	2.48	1.45	0.79	0.25	4.98
	wt. %	0.20	49.80	29.12	15.86	5.02	100.00
FMT1	weight (g)	0.01	2.18	1.30	1.02	0.25	4.76
	wt. %	0.21	45.80	27.31	21.43	5.25	100.00
FMT2	weight (g)	0.01	2.70	0.93	1.12	0.25	5.01
	wt. %	0.19	53.90	18.56	22.35	5.00	100.00
FMT3	weight (g)	0.01	2.53	1.03	1.22	0.22	5.01
	wt. %	0.20	50.49	20.56	24.35	4.40	100.00

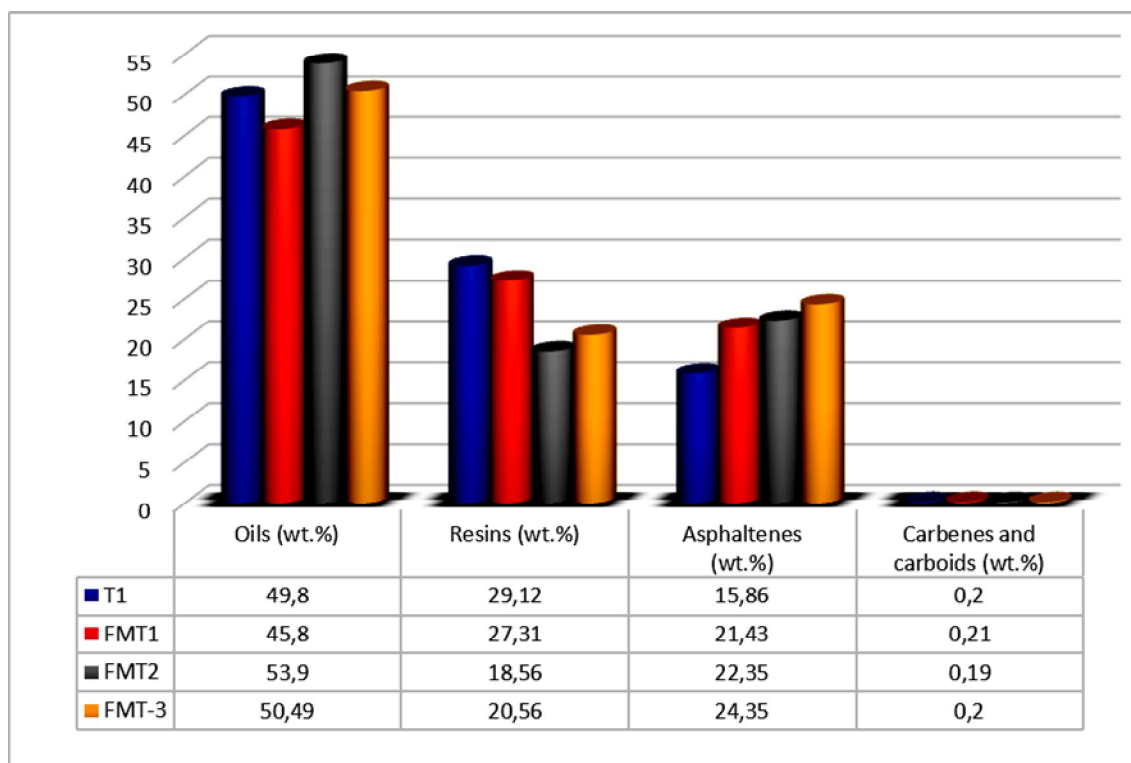


Fig. 4. Group hydrocarbon composition of T1 and FMT

The findings in Table 3 and Fig. 4 indicate that oils practically do not react in the condensation process with formaldehyde. In our opinion, the main reactions in the modification process occur with resins, which are transformed into asphaltenes, as evidenced by a decrease in the content of resins and an increase in the content of asphaltenes. The constant content of carbenes and carboids with an increase in the content of the modifier (formaldehyde) in the modification process implies that they do not participate in the modification process and they are not formed from asphaltenes either. That is, the chemistry of the modification process is related to the transformation of resins and asphaltenes, as it should be expected since these groups of raw materials (T1) contain heteroatom functional groups (for example, hydroxyl) that are more prone to condensation with formaldehyde. To confirm this, FTIR spectra of oils (Fig. 5), resins (Fig. 6), and asphaltenes (Fig. 7) obtained from T1, FMT1, FMT2, and FMT3 were recorded.

Analysis of the spectra of the oil fraction of both original and modified products (Fig. 5) indicates that the oil fractions contain a small amount of aromatic compounds (band 1600 cm^{-1} , oscillations of the aromatic ring). These aromatic compounds contain methyl substituents, as indicated by the absorption band at 1461 cm^{-1} , and are bonded by $-\text{CH}_2-$ moieties (1376 cm^{-1}). Moreover, there may be 2 or more $-\text{CH}_2-$ groups, as indicated by the ab-

sorption band at 720 cm^{-1} . The absorption band at 812 cm^{-1} , which can be attributed to the deformation vibrations of the CH group, indicates that such oil fractions contain, in a small amount, 1,3-disubstituted benzene rings. Trisubstituted benzene rings in all samples are proven by the presence of absorption bands at 840 cm^{-1} .

Hence, it can be concluded that there are no condensation products of arenes with formaldehyde in the oil fractions, which confirms the assumptions made earlier.

compounds. The aromatic compounds contain CH_2 and CH_3 groups in their composition, which is confirmed by absorption bands at 1455 and 1375 cm^{-1} .

At the same time, in the spectra shown in Fig. 6, in contrast to the spectra presented in Fig. 5, an absorption band appears at 1260 cm^{-1} . This band was found in both resins isolated from T1 and resins modified with different amounts of formaldehyde. This indicates that the selected resins contain compounds that contain oxygen atoms formed as a result of the condensation of arenes with formaldehyde. The fact that the absorption band at 1260 cm^{-1} is the total content of oxygen-containing compounds, which are both in the original sample T1 and in the condensation products of arenes with formaldehyde, is indicated by the data shown in Fig. 7. In accordance with Fig. 7, in samples with a formaldehyde content of 2 and 3 % in asphaltenes, this absorption band almost disappears. A plausible explanation for this is that, under the

modification conditions, a further transformation of modified products occurs with the release of free formaldehyde, which leads to the disappearance of oxygen-containing fragments.

Absorption bands at 1600 cm^{-1} were detected in all resin samples (Fig. 6), which indicates the presence of aromatic

The absorption band at 1090 cm^{-1} detected in the spectra of the samples (Fig. 6) indicates the presence of monosubstituted benzene derivatives, while, as the spectra show, with an increase in the amount of formaldehyde used for the reaction, their intensity decreases, which confirms the chemical interaction between arenes and formaldehyde.

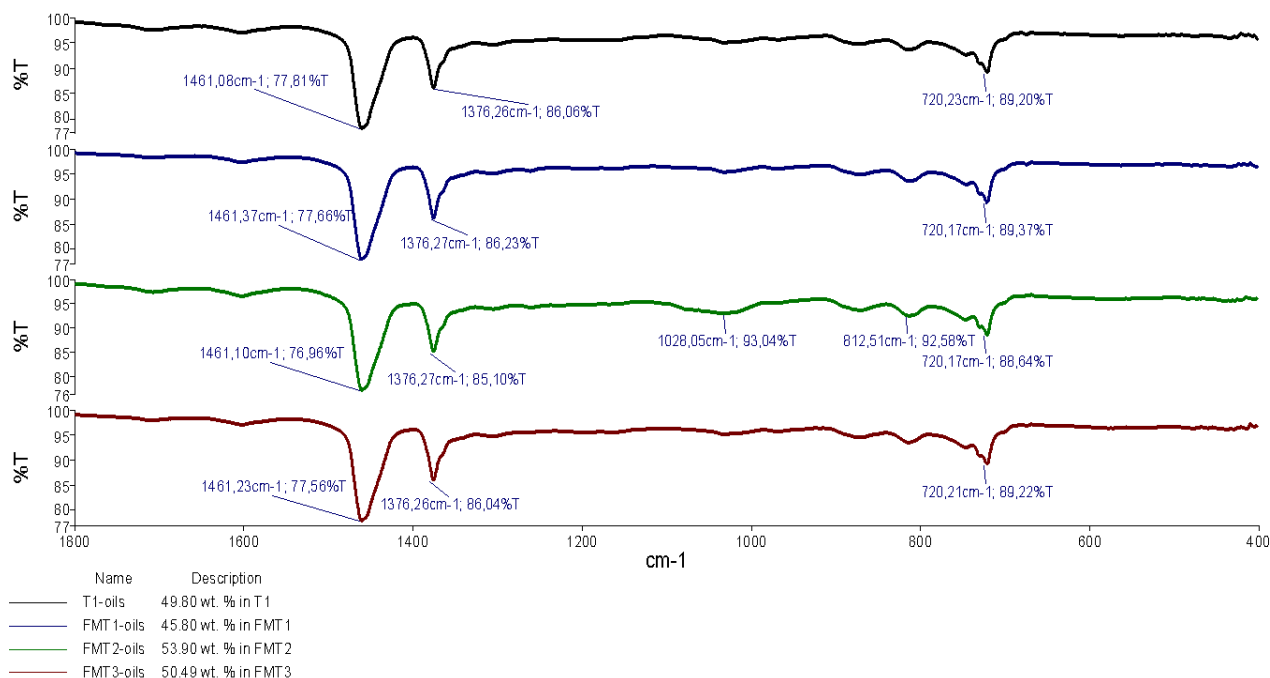


Fig. 5. FTIR spectra of oils

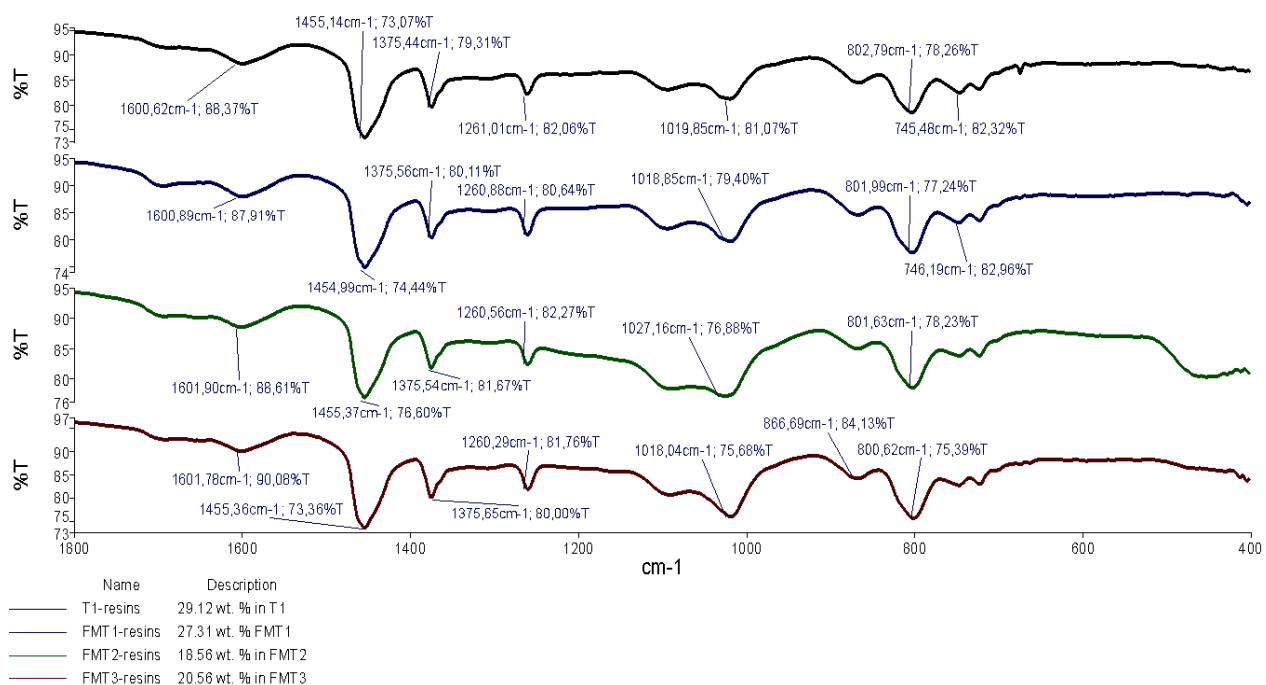


Fig. 6. FTIR spectra of resins

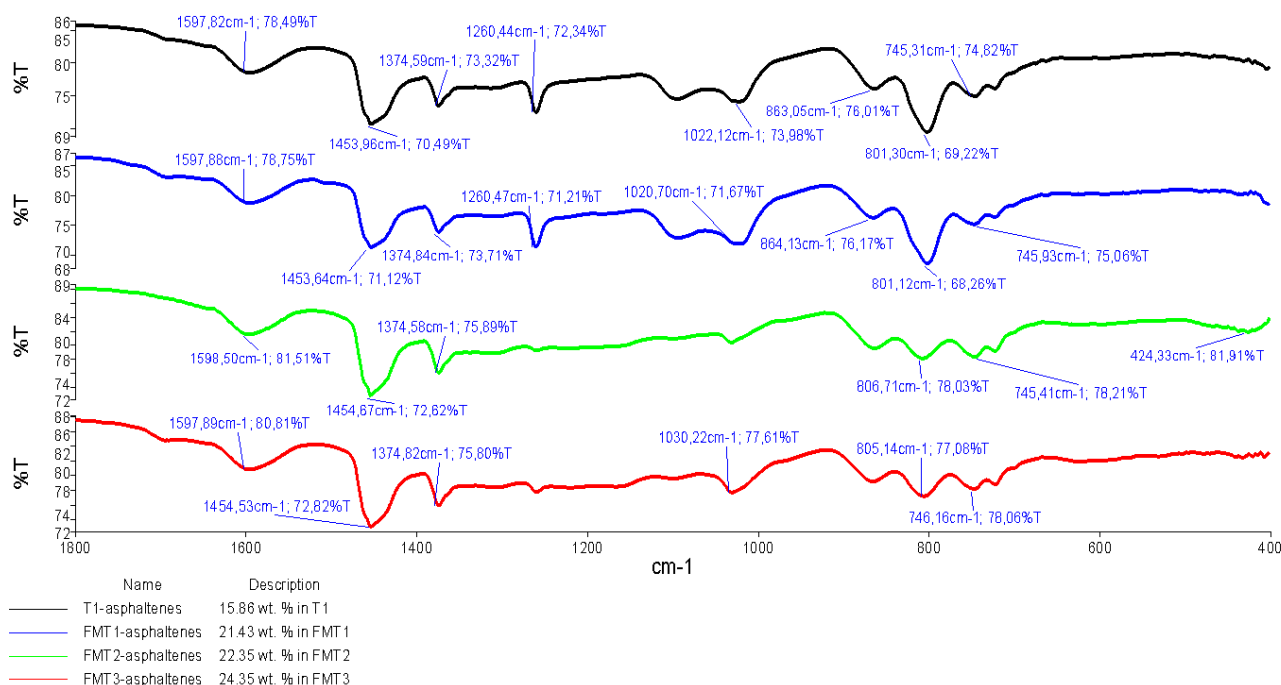


Fig. 7. FTIR spectra of asphaltenes

Similar to the absorption band at 1260 cm^{-1} , a decrease in the intensity of the absorption band at $1027\text{--}1018\text{ cm}^{-1}$ indicates deeper chemical transformations in the structure of the samples.

In all the samples, an absorption band at $802\text{--}800\text{ cm}^{-1}$ was detected, which indicates the presence of *meta*-disubstituted benzene derivatives in the resins.

A band at 460 cm^{-1} in the spectrum of the sample modified with 2 % formaldehyde evidenced the presence of *ortho*- and *meta*-disubstituted benzene derivatives in the structure.

In all the spectra shown in Fig. 7, absorption bands at $1598\text{--}1597\text{ cm}^{-1}$ were found which indicate the presence of substituted aromatic compounds. All of them contain CH_2 and CH_3 groups, as indicated by absorption bands at $1454\text{--}1453\text{ cm}^{-1}$.

Oxygen atoms, which are included in the structure of asphaltenes, were found only in the original T1 and the modified sample containing 1 % formaldehyde (1260 cm^{-1}). In the samples with formaldehyde content of 2 and 3 %, these bands are of low intensity, which implies deep transformations of the obtained modified products with the release of formaldehyde.

In the samples with 2 and 3 % formaldehyde, there are no absorption bands at 1094 cm^{-1} , which indicate the absence of mono-substituted benzene. Deep transformations of modified products are also confirmed by the absorption bands at $1030\text{--}1020\text{ cm}^{-1}$.

As the amount of the modifier increases, the intensity of the absorption band at $864\text{--}863\text{ cm}^{-1}$ decreases, that corresponds to tetra-substituted benzene derivatives and indicates the asphaltene structure formation.

4. Conclusions

It has been shown that with an increase in the flow rate of the modifier (forming mixture – formalin and sulfuric acid) in the process of tar modification, the product viscosity increases, as evidenced by a decrease in penetration at 298 K (from 247 to 47 dmm) and an increase in the softening temperature (from 312 to 356.4 K). This modification process can replace the traditional processes of obtaining bituminous materials with the required operational properties – oxidation and high-temperature distillation of tars and modification of bitumen with polymers. By determining the group hydrocarbon composition of the obtained bitumens and FTIR studies of these groups of hydrocarbons (oils, resins and asphaltenes), the main structural transformations that occur during the modification process have been revealed. The main components involved in the condensation reaction with formaldehyde are highly condensed arenes, especially those with functional groups, such as hydroxyl. Such hydrocarbons are mainly present in resins and asphaltenes of the raw material of the process (tar). Carbenes and carboids are not formed upon the modification process, which is positive for the bituminous materials prepared, as they impair the

low-temperature properties of the binding material. The FTIR studies of oils produced from tars modified with formaldehyde showed that they lack condensation products of arenes with formaldehyde, which indicates that the oils practically do not react in the modification process.

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ВИРОБНИЦТВО БІТУМУ, МОДИФІКОВАНОГО НИЗЬКОМОЛЕКУЛЯРНИМИ ОРГАНІЧНИМИ СПОЛУКАМИ ІЗ НАФТОВИХ ЗАЛИШКІВ. 7. ДОСЛІДЖЕННЯ СТРУКТУРИ ГУДРОНІВ, МОДИФІКОВАНИХ ФОРМАЛЬДЕГІДОМ

Анотація. Хімічним модифікуванням гудрону формальдегідом з використанням як каталізатора сульфатної кислоти отримано три зразки бітумного матеріалу з різними температурами розм'якшення 321, 332 і 356,4 К. Визначено ґруповий вуглеводневий склад сировини процесу модифікації (гудрону) та отриманих бітумів. Також здійснено FTIR-дослідження одержаних груп вуглеводнів (олив, смол та асфальтенів). Досліджено структурні перетворення та запропоновано можливий хімізм процесу модифікування гудрону формальдегідом.

Ключові слова: гудрон, бітум, формальдегід, хімічне модифікування.