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Study Of The Composition Of The Secondary Product Of The Pyrolysis Process And The Synthesis Of Polymethylene-Anthracenesulphoxicolate

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Summary: Today, the Ustyurt gas chemical plant in our Republic is not processing a large amount of by-product waste, which has a negative influence on the environment. The composition of these wastes was studied by vacuum fractionation at high temperature, and the obtained products were analyzed by physico-chemicall. Polymethyleneanthacene sulfoacids (SOF-1 and SOF-2) with a spatial structure were synthesized by polycondensation of the obtained mono- and dianthracene sulfoacids with formalin. Process parameters were studied.

Key Words: pyrolysis, secondary product, chemical composition, anthracene, sulfoacids, polymethyleneanthracene sulfoacid, chromato-mass spectrum, IR spectrum, SEM, TG and DTA analysis.

As a result of the development of the oil and gas chemical industry the number of enterprises producing polymer products based on natural gas is increasing in our country. One of them is the Ustyurt gas-chemical complex belonging to "Uz-KorGas Chemical" LLC, which produces 3 mln. per year from the "Surgul" mine. m^3 of natural gas and more than 115,000 tons of gas condensate are extracted. Natural gas is separated into methane, ethane and propane-butane fractions; methane as a finished product, ethane, propane-butane fractions are pyrolyzed separately; ethylene and propylene are then polymerized into granulated polyethylene and polypropylene. The annual capacity of the complex is 387,000 tons of polyethylene, 83,000 tons of polypropylene, and secondary products: 102,000 tons of pyrolysis disaryl, 8,000 tons of pyrolysis oil and 10,000 tons of tar products. These secondary products are not processed in the complex and at low prices. poor quality fuel, steam is used as boiler fuel.

Tar-product is an odorless, black secondary product, its physico-chemical properties are listed [2-6].

The composition of the fractions was determined by chromato-mass-spectroscopy method. [2-6].

It was found that fraction with 320-360^{0}C contain polycyclic aromatic hydrocarbons. In particular, it was determined that 38,64% of phenanthrene was present in the interval 15,824-15,942 minutes and 93% similarity compared to the base, and 10,55% anthracene was present in the interval 16,649-16748 minutes and 98% similarity compared to the base [2-6].

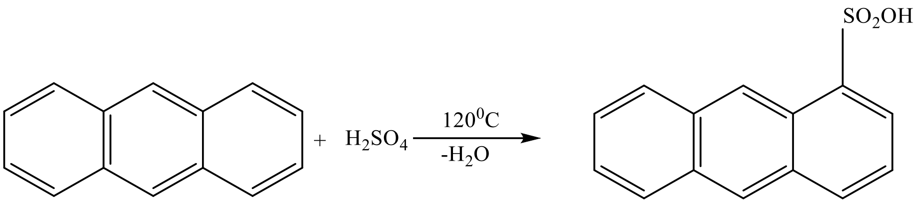
Anthracene sulfoacids are solid substances with a melting temperature in a certain range, they are well soluble in water, poorly soluble in organic solvents. In the process of anthracene sulfonation, unlike halogenation and nitration, α and β-anthracene sulfoacids are formed.

Compared with naphthalene, the interaction of anthracene with electrophilic reagents mainly goes to the 9th and 10th states, that is, the meso-state. Quantum-chemical calculations show that the meso-states have a high electron density and electrophilic exchange. When anthracene is treated with oleum in acetic acid solution, equal amounts of 1- and 2-sulfonic acids are formed. As a result of sulfation with 75% H_2SO_4 at 100^{0}C, the 2-sulfoacid is formed and the addition of mercury shifts the sulfo group to the 1st state.

The reaction initially produces 9-anthracenesulfoacid as a primary product and then, during of desulfation, it was formed 1- and 2-anthracenesulfoacids, which are thermodynamically stable.

Discussion of results. As the temperature and duration of the reaction have been increased, the formation of a mixture of 2-sulfoacids and disulfoacids from 1-sulfoacid also was increased.

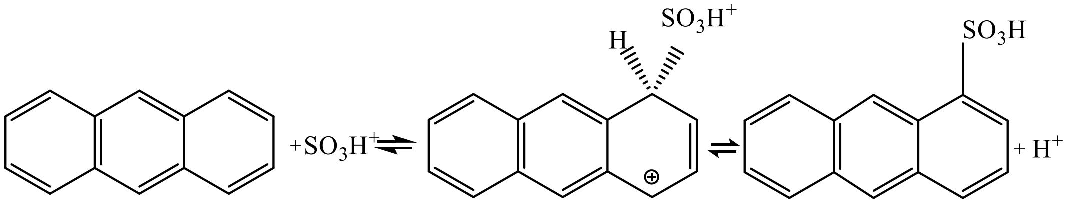
The process reaction is as follows:



The mechanism of the reaction[8]:

a. $2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$

b. $H_3SO_4^+ \rightleftharpoons SO_3H^+ + H_2O$



Control of the sulfonation process determines the completion of the reactions, the composition of the sulfoacids formed and the concentration of sulfuric acid.

The total amount of sulfoacids formed in the reaction mixture is determined according to the following scheme:

1) titration determines the total amount of acids (sulfonic and sulfuric acids);

2) the amount is determined by precipitation of sulfuric acid;

3) the amount of sulphonic acids is determined by the difference between the amount of total acid and the sulfuric acid.

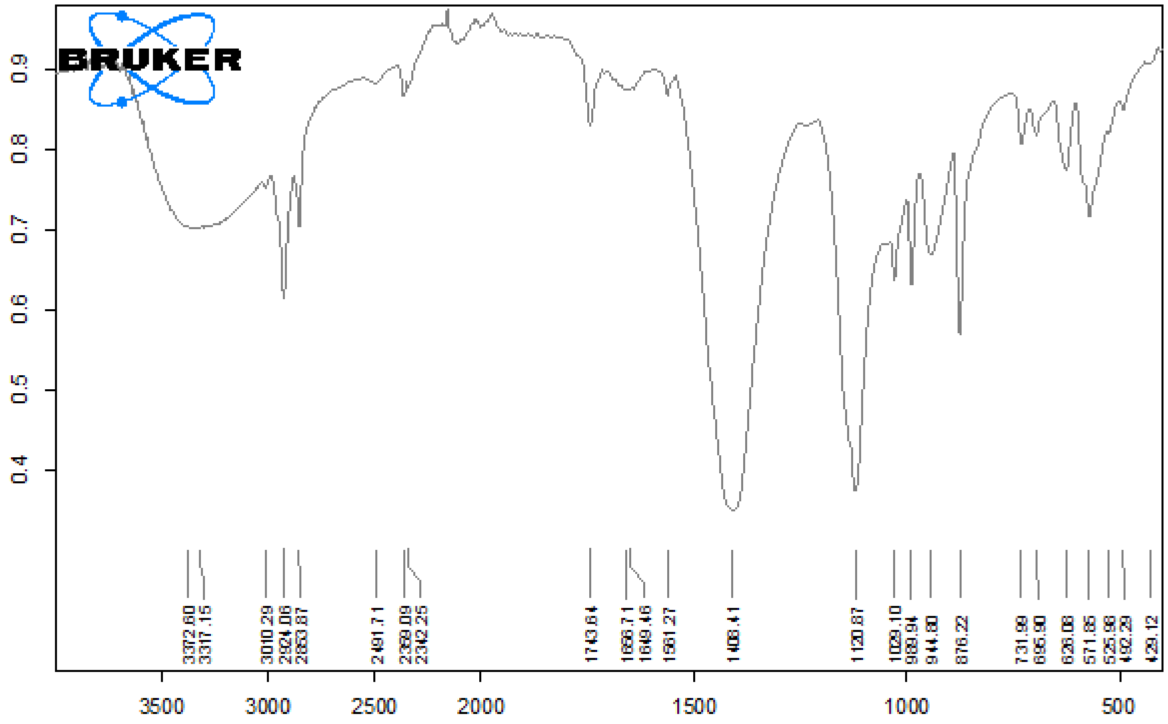


Figure 1. IR-spectrum of 1-anthracene sulfonate sodium.

Table 1

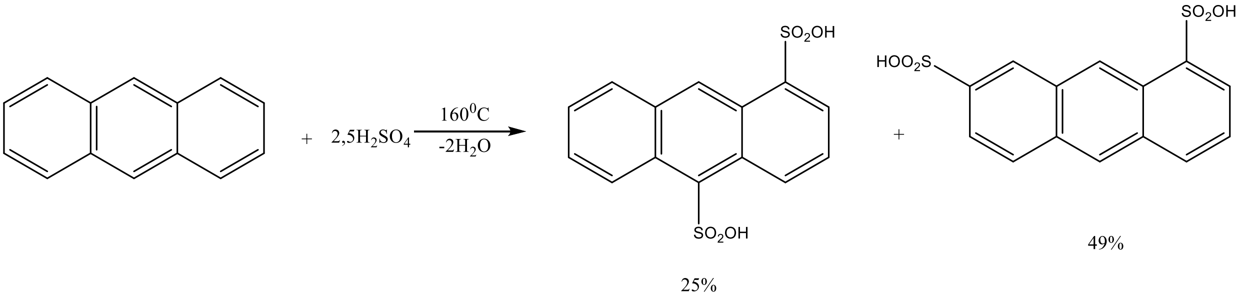
IR-spectral analysis of sodium 1-anthracenesulfonate

Vibration frequency, sm^{-1}	Functional group	Oscillating
3010,29	-C-H in the aromatic nucleus	valence vibration
1561,27	C=C in the aromatic nucleus	valence vibration
1656,71	aromatic nucleus	valence vibration

1120,87	$-SO_3Na$	valence vibration

Research on the synthesis of anthracene disulfoacids

Anthracene is formed in the presence of concentrated sulfuric acid at a high temperature above 160^0C at the synthesis of disulfoacids. When the duration of the process is 4-8 hours a mixture of 1,5- and 1,8-anthracenesulfoacids is formed. The reaction equation is as follows:



Anthracenesulfoacids contained in sulfomasa were isolated according to the following sequence:

1) calcium hydroxide is added to sulfomasa. The reason for this is the loss of excess sulfuric acid in the form of calcium sulfate. Excess sulfuric acid is neutralized with calcium hydroxide, precipitates and the precipitate is filtered;

2) at adding sodium carbonate to the filtrate the calcium salt of anthracene disulfonic acid is converted to the sodium salt, and the excess calcium hydroxide is precipitated as calcium carbonate. The resulting mixture is filtered again;

3) the aqueous solution of sodium 1,5-anthracene disulfonate and sodium 1,8-anthracene disulfonate, synthesized and purified from by-products of the reaction, is purified from water using a vacuum evaporator.

The following reactions occur in the above processes:

$$C_{14}H_{10} + 2H_2SO_4(\text{kons}) \rightarrow C_{14}H_8(SO_3H)_2 + 2H_2O$$

$$C_{14}H_8(SO_3H)_2 + 2Ca(OH)_2 + H_2SO_4 \rightarrow Ca(C_{14}H_8(SO_3)_2) + CaSO_4\downarrow + 4H_2O$$

$$Ca(C_{14}H_8(SO_3)_2) + Ca(OH)_2 + 2Na_2CO_3 \rightarrow C_{14}H_8(SO_3)Na_2 + 2NaOH + 2CaCO_3\downarrow$$

Synthesized sodium 1,5-and 1,8-sodium disulfonated were separated from each other by adsorption chromatography. For this purpose a small amount of cotton was placed at the bottom of the chromatographic column (length 2 m, diameter 4 cm) and it was placed on a tripod in a vertical position. Then 3/4 of the chromatographic column is filled with silica gel adsorbent of the same size. For this, put silica gel and solvent (water) in the flask were shaked well. Then the resulting suspension is poured into the column little by little, and the column is periodically hit with a thick piece of vacuum rubber to ensure good placement of the adsorbent. The adsorbent stuck to the column wall is washed off with solvent (water). The sulfonate solution is gradually added to the column filled with adsorbent, the column is washed with solvent (water). The flow rate of the solvent from the column is controlled using a tap, in which the speed of the solvent flowing from the column should not exceed 30-40 drops/min. In the result of washing, the formed products as a result of the reaction begin to separate from each other and form rings. In this, the sulfonates began to separate from each other. First, each washed part was divided into fractions, dried and weighed. As a result, 1,5-anthracenesulfonate sodium (μ=25%), 1,8-anthracenesulfonate sodium (μ^1=49%) were obtained. The IR spectrum of the synthesized 1,8-anthracenesulfonic acid was obtained and analyzed.

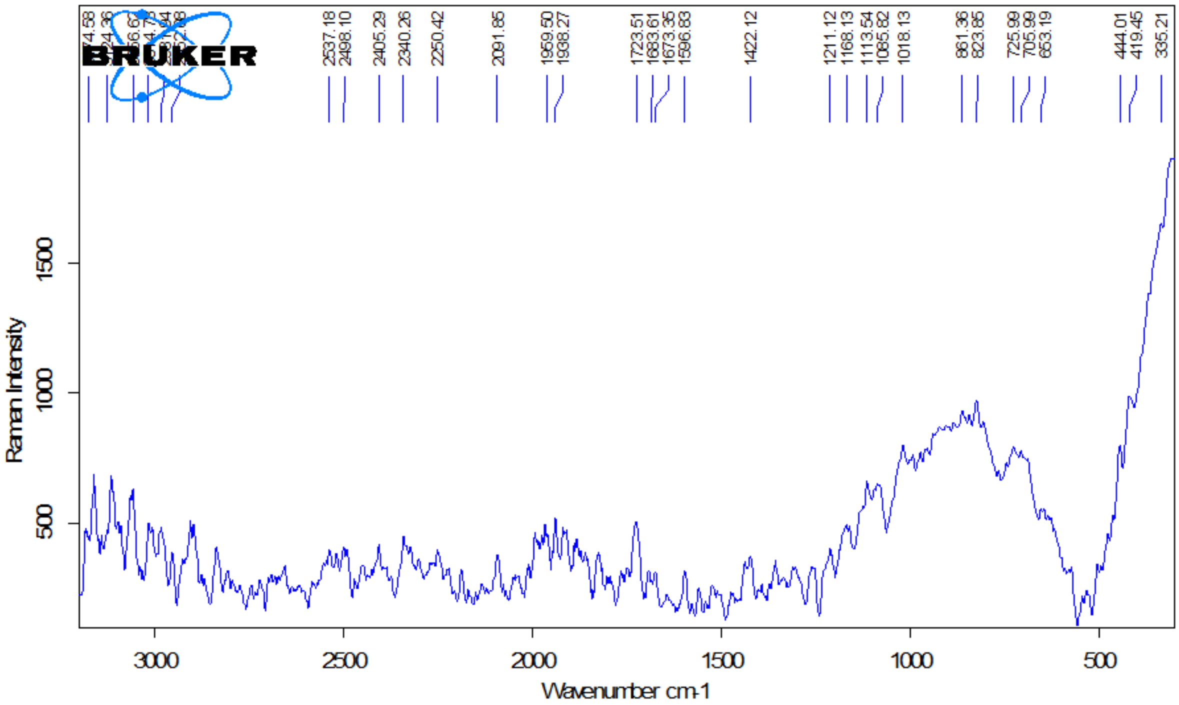


Figure 2. Infrared spectrum of the sodium salt of 1,8-anthracene disulfoic acid

Table 2

Analysis of the infrared spectrum of the sodium salt of 1,8-anthracene disulfoic acid

Vibration frequency, sm^{-1}	**Functional group**	**Form of vibration**
3056,65	-C-H in the aromatic nucleus	valence vibration
1596,83	C=C in the aromatic nucleus	valence vibration
823,85	aromatic nucleus	valence vibration
1168,13	-SO_3Na	valence vibration

Synthesized anthracenesulfoacids were used for synthesize of polymethyleneanthracenesulfoacid with spatial structure.

Technological parameters of the process of synthesis of polymethyleneanthracenesulfoacid based on anthracene isolated from the secondary "tar product" of Uz-KorGas Chemical LLC were studied. Polymethyleneanthracenesulfoacid (SOF-1) was synthesized by polycondensation of anthracenesulfoacid 1 with formalin. polymethyleneanthracenesulfoacid (SOF-2) was synthesized as a result of polycondensation of anthracenesulfoacids with formalin.

The following processes were carried out for the synthesis of SOF-1:

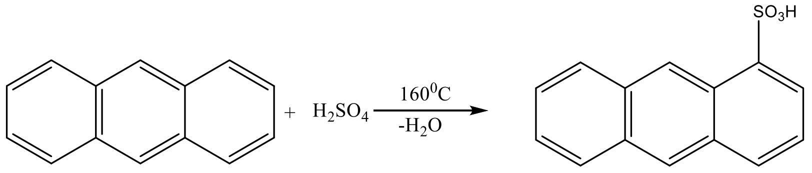
1. anthracene was separated and purified from the fraction between 320-360^{0}C obtained by vacuum extraction and then fraction extraction;

2. then, anthracene was sulfonated using concentrated sulfuric acid (mol ratio 1:1.5) at 160^{0}C for 6 hours, as a result a dark black sulfomasse was obtained (reaction 1);

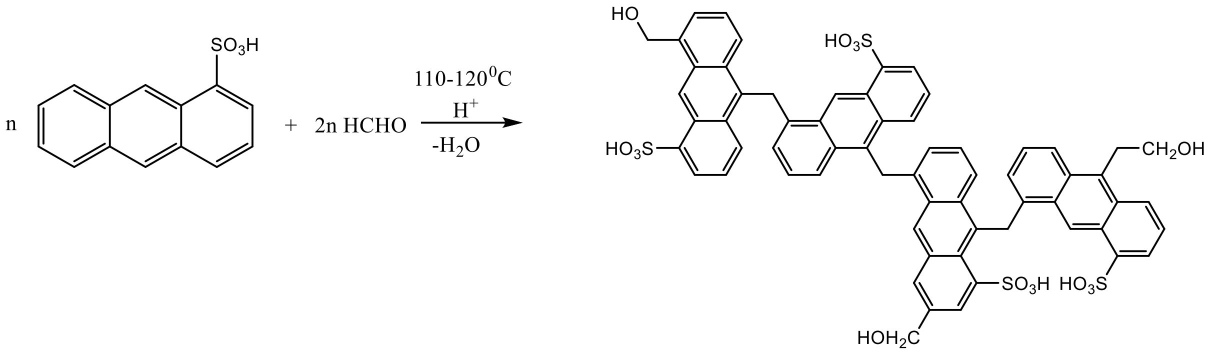
3. the resulting sulfoma mass was placed in a vessel working under pressure and polycondensed with 35% formalin (initially anthracene and formaldehyde mole ratio 1:2.1) at 110-120^{0}C and a pressure of 35 atm (reaction 2);

4. The synthesized polycondensate was cooled and mechanically crushed and heated at 95-100^{0}C for 18-24 hours to complete the polycondensation (reaction 3);

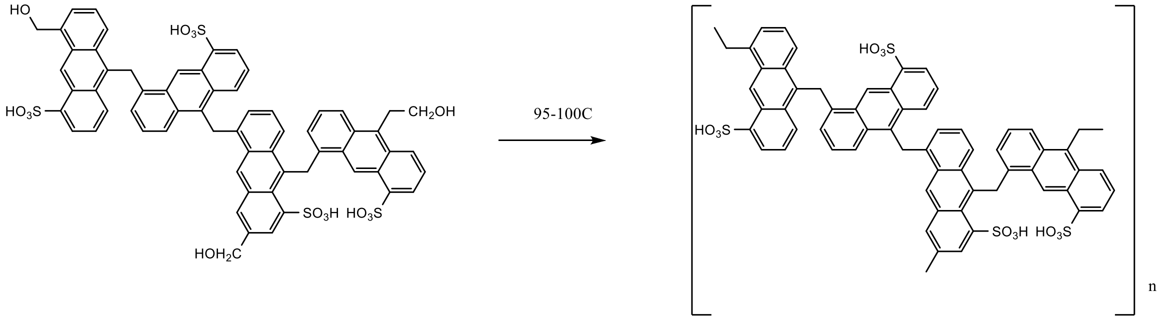
Reaction 1:



Reaction 2:



Reaction 3:



The reaction mechanism is as follows:

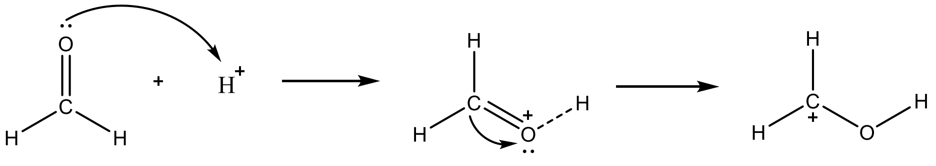
1. H+ is formed as a result of dissociation of sulfuric acid.

$$H_2SO_4 + H_2O \rightleftharpoons HSO_4^- + H_3O^+ \qquad \text{I.}$$

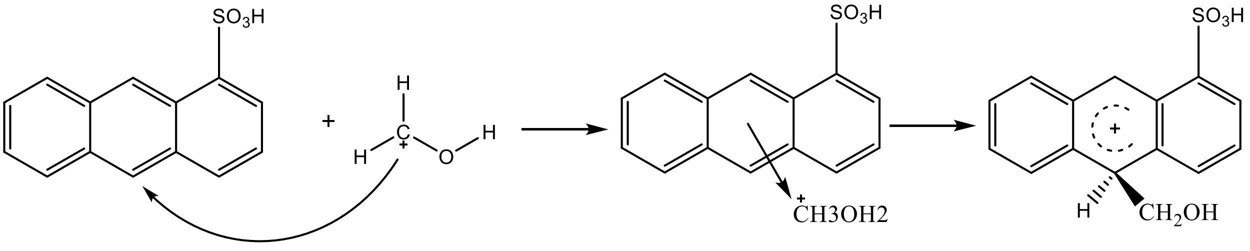
$$H_2SO_4 + H_2SO_4 \rightleftharpoons HSO_4^- + H_3SO_4^+ \qquad \text{II.}$$

$$H_3SO_4^+ \rightleftharpoons H_2SO_4 + H^+ \qquad \text{III.}$$

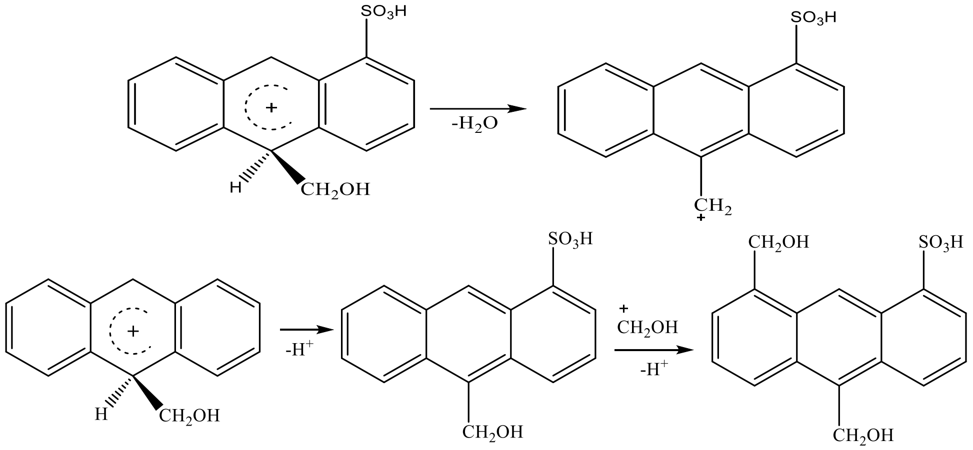
2. The resulting H+ cation combines with formaldehyde to form +CH_2OH hydroxymethylene carbocation.



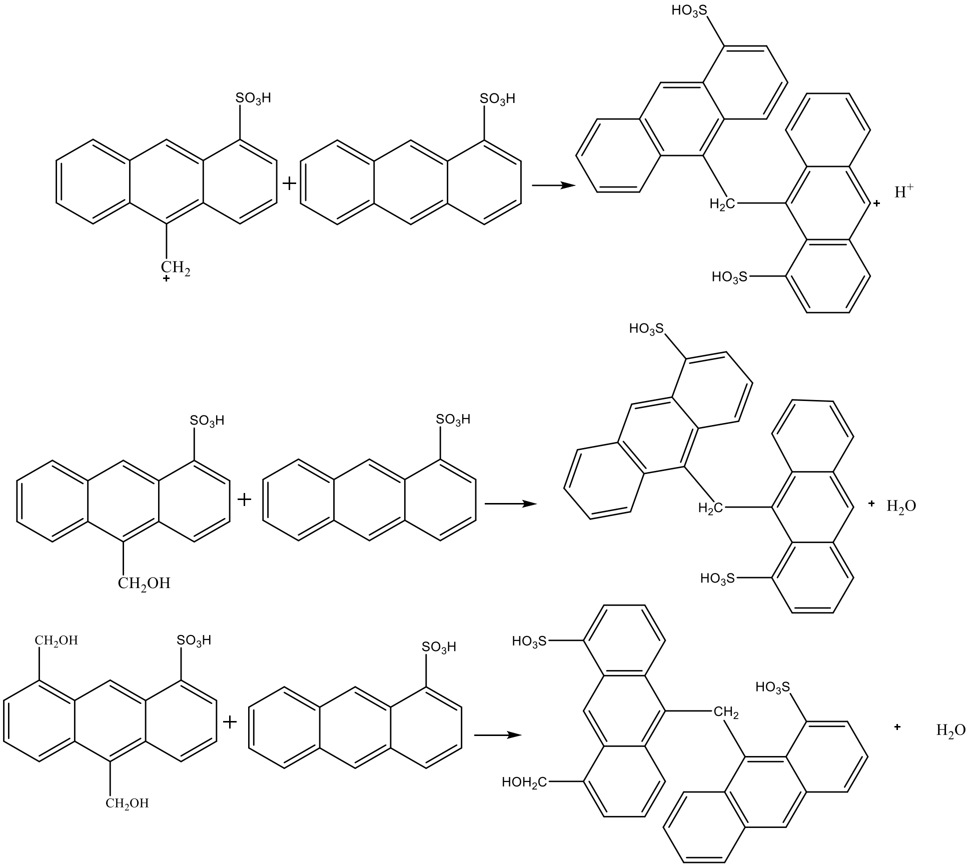
3. The hydroxymethylene carbocation interacts with the 5th carbon atom in the 1-anthracene sulfonic acid with formation first a p-complex and then a s-complex. In the Gaussian program, it was determined that the 5th carbon atom of the 1st anthracene sulfoacid has a strong negative charge of -0,229, the 6th carbon atom -0,144, the 9th carbon atom -0,146, and the 10th carbon atom – 0,194. Therefore, electrophilic reactions were carried out with respect to carbon atoms 5, 6, 9 and 10.



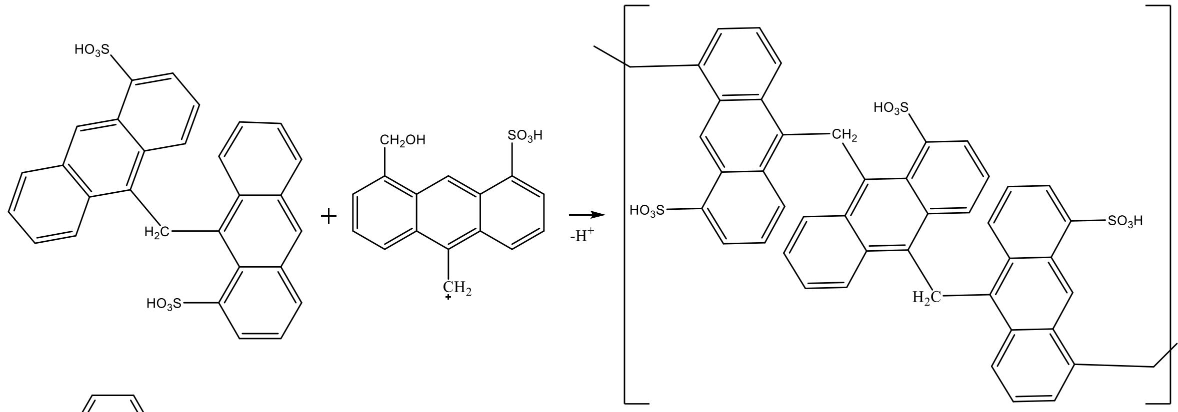
4. Carbocation and alcohol are formed as a result of release of water or H^+ from the obtained s-complex.

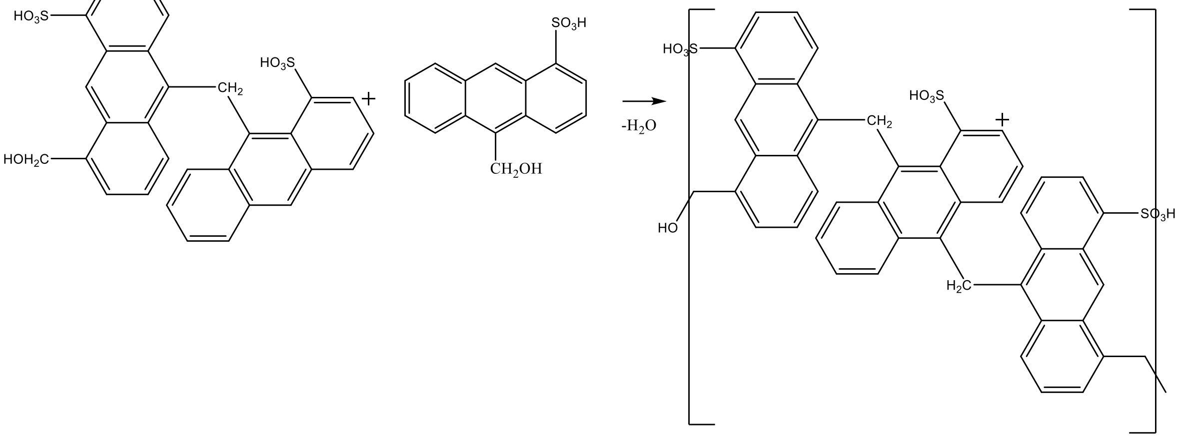


5. Reaction of carbocation and alcohol with 1-anthracene sulfonic acid forms dimer and H+ and H_2O.

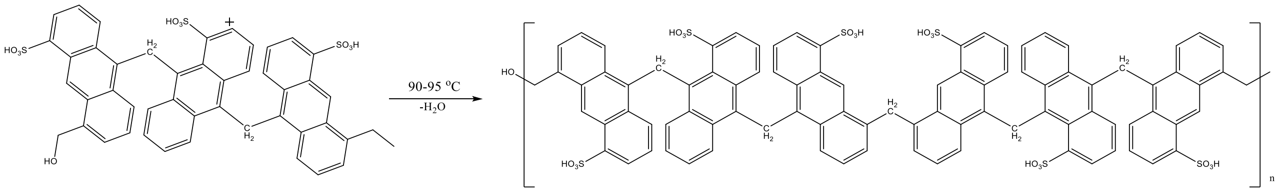


6. Oligomers are formed by reaction of dimer with carbocations or alcohols.





7. As a result of heating the obtained oligomers at 90-95^{0}C for 12 hours polymethyleneanthracenesulfonic acid with spatial structure was formed as a result of their mutual polycondensation:



The operational properties of spatially salted polymethyleneanthracenesulfonic acid have been depended on the mole ratio of substances, the duration of the polycondensation process, and the temperature.

Table 3

SOF-1 synthesis process parameters (t=100-110^{0}C)

Mole ratio of 1-anthracene sulfo-acid to formaldehyde	Reaction time, hours	Total COE, mg-eq/cm^3	Relative volume, cm^3/g
1:0,8	2	0,42	9,0
	3	0,41	8,85
	4	0,43	8,9
	5	0,43	8,95
	6	0,22	8,1
1:0,9	2	0,5	8,6
	3	0,51	8,55
	4	0,51	8,8
	5	0,52	8,7
	6	0,5	8,6

1:1,0	2	0,6	8,1
	3	0,62	8,2
	4	0,62	8,1
	5	0,6	8,05
	6	0,61	8,0
1:1,1	2	0,65	7,9
	3	0,61	7,8
	4	0,60	7,8
	5	0,60	7,8
	6	0,59	7,6
1:1,2	2	0,42	7,5
	3	0,41	7,3
	4	0,43	7,1
	5	0,43	7,0
	6	0,22	7,0
1:1,3	2	0,5	6,8
	3	0,51	6,7
	4	0,51	6,6
	5	0,52	6,5
	6	0,5	6,5
1:1,4	2	0,6	6,4
	3	0,62	6,3
	4	0,62	6,2
	5	0,6	6,0
	6	0,61	6,0
1:1,5	2	0,65	5,8
	3	0,61	5,7
	4	0,60	5,5
	5	0,60	5,4
	6	0,59	5,4
1:1,6	2	0,65	5,2
	3	0,69	5,1
	4	0,73	5,1
	5	**0,85**	**5,0**
	6	0,75	5,0
1:1,7	2	0,65	5,2
	3	0,61	5,3
	4	0,60	5,5
	5	0,60	6,0
	6	0,59	6,0

The following processes were performed to synthesize SOF-2:

1. the secondary product of the pyrolysis process anthracene was extracted and purified by fractional extraction under vacuum and then under normal pressure;

2. the obtained anthracene was sulfonated using concentrated sulfuric acid (mol ratio 1:2) at 160-165^{0}C for 8 hours, as a result, a dark black sulfomasse was obtained;

3. the resulting sulfoma mass was placed in a pressure vessel and polycondensed with 35% formalin (initially, the mole ratio of anthracene and formaldehyde was 1:2) at 110-120^{0}C and a pressure of 30-40 atm;

4. the synthesized, water-insoluble solid polycondensate was washed by mechanical grinding and heated at 90-95^{0}C for 12 hours to complete the polycondensation.

The properties of spatially salt polymethyleneanthracene sulfonic acid obtained as a result of the reaction depend on the duration of the polycondensation process.

Table 4

SOF-2 synthesis parameters (t=100-110^{0}C, P=const)

Mole ratio of anthracene sulfo-acids and formaldehyde	Duration of reaction, hour	COE, mg-ekv/sm^3	Relative volume, cm^3/g
1:1,2	2	0,41	7,1
	3	0,42	6,8
	4	0,41	6,9
	5	0,42	6,9
	6	0,42	7,1
1:1,4	2	0,52	6,7
	3	0,51	6,5
	4	0,51	6,8
	5	0,52	6,8
	6	0,50	6,6
1:1,6	2	0,61	6,1
	3	0,62	6,2
	4	0,62	6,1
	5	0,62	6,0
	6	0,60	6,0
1:1,8	2	0,72	5,6
	3	0,73	5,8
	4	0,75	5,8
	5	0,75	5,8
	6	0,68	5,6
1:2	2	0,85	5,1
	3	0,84	5,2
	4	1,044	4,6
	5	0,86	5,2
	6	0,75	5,3

In the process of polycondensation, the increase in pressure serves to increase the molecular mass of the obtained spatial polymer.

IR-spectrums of SOF-1 and SOF-2 polymethyleneanthracenesulfoacids synthesized on the basis of anthracene obtained from the secondary product of the pyrolysis process "Tar-product" were obtained and analyzed.

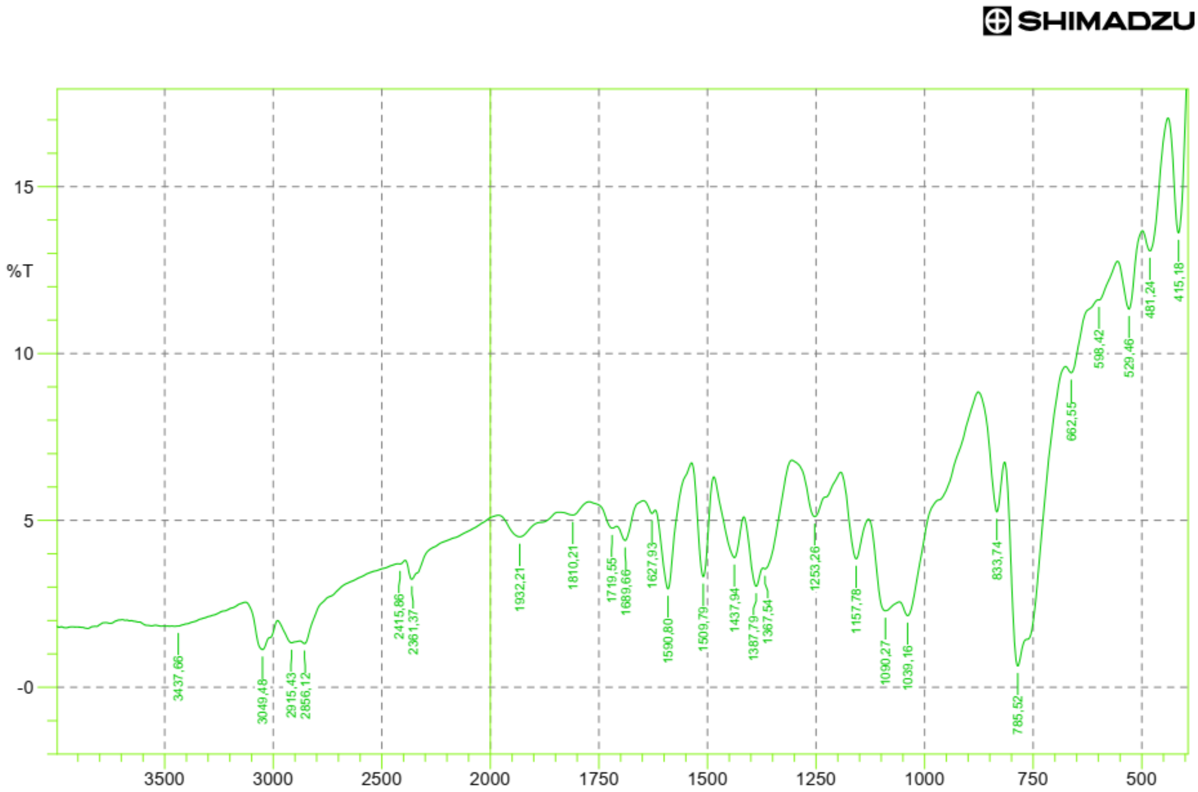


Figure 3. IR-spectrum of SOF-1 polymethylenenaphthalene sulfonic acid

Table-5

Analysis of the IR spectrum of SOF-1 polymethylenenaphthalene sulfonic acid

Vibration frequency, sm^{-1}	Functional group	Type of vibration
3437,66	-OH	valence
3049,48	C-H in the aromatic nucleus	valence
2915,43	-CH$_2$-	asymmetric valence
2856,12	-CH$_2$-	symmetric valence
1437,94	-CH$_2$-	deformation
1157,78	S=O	valence
1039,16	-SO$_3$H	Valence
786,52	C-H in the aromatic nucleus	deformation
1590,2	substituted aromatic nucleus	valence vibration
1689,66	aromatic nucleus	valence
1325,59	-OH	Deformation

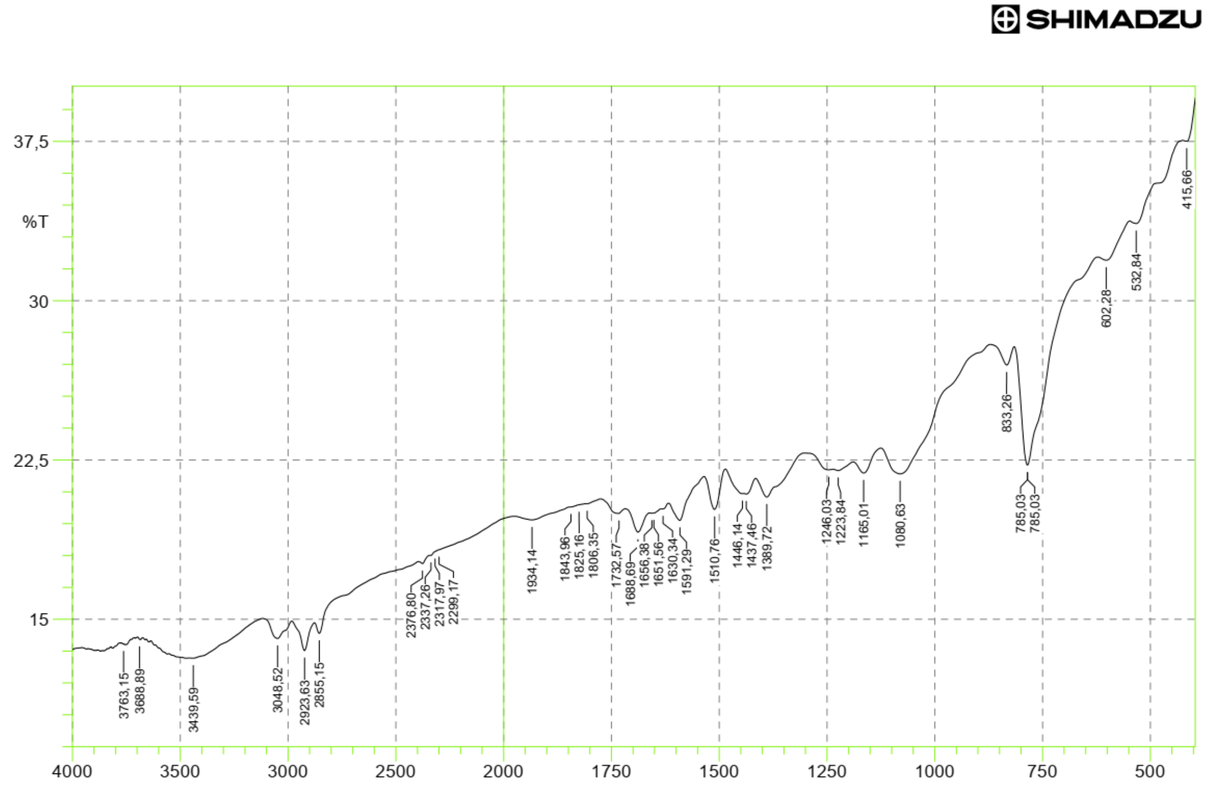


Figure 4. IR-spectrum of SOF-2 polymethylenenaphthalene sulfonic acid

Table-6

Analysis of the IR spectrum of SOF-2 polymethylenenaphthalene sulfonic acid

Vibration frequency, sm^{-1}	Functional group	Type of vibration
3439,59	-OH	valence
3048,52	C-H in the aromatic nucleus	valence
2923,63	$-CH_2-$	asymmetric valence
2855,15	$-CH_2-$	asymmetric valence
1446,14	$-CH_2-$	deformation
1165,01	S=O	valence
1080,63	$-SO_3H$	valence
833,26	C-H in the aromatic nucleus	deformation
1510,76	substituted aromatic nucleus	valence
1389,72	-OH	deformation

SEM (scanning electron microscope) was used to determine the surface morphology and element composition of the synthesized polymethyleneanthracene sulfoacid with spatial structure SOF-2.

The results of SEM analysis of SOF-1polymethyleneanthracene sulfoacid are presented in Figures 3.12. According to the results of the analysis, it contains macropores and the element composition of SOF-1 consists of 67,9% C, 21,2% O and 10,9% S.

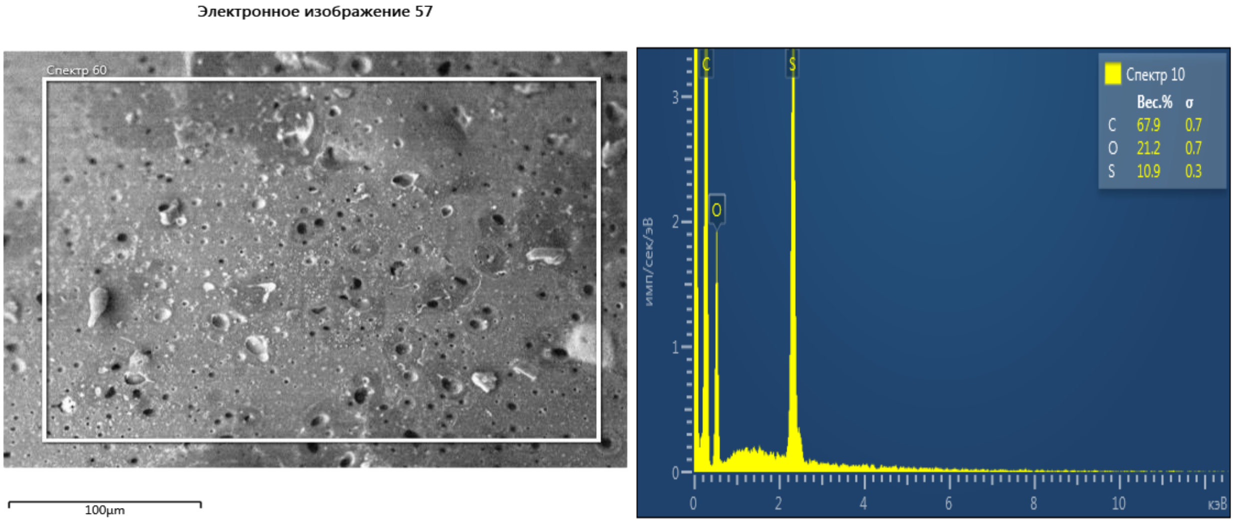


Figure 5. Surface structure and element composition of SOF-2.

The results of SEM analysis of SOF-2 polymethyleneanthracene sulfoacid are presented in Figures. According to the analysis, it contains macropores from 120 to 650 µm. The elemental composition of SOF-2 consists of 68,3% C, 18,1% O and 12,7% S.

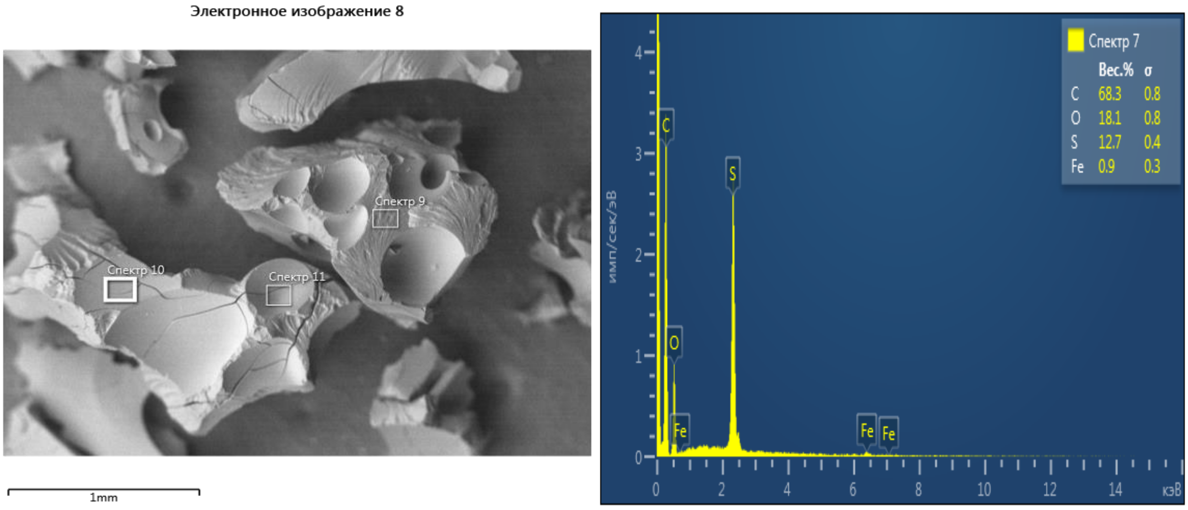


Figure 6. Surface structure and element composition of SOF-2.

Thermal stability of SOF-2 was studied by thermogravimetric analysis (TGA) method. Thermogravimetric analysis with mass loss in two stages, the first is 20,009% in the range of 23,58-205,00^{0}C, and the second stage is 20,495% in the range of 205,00-543,72^{0}C, 543,72-801,7 and up to 15,259% mass of matter decreased. It was determined that the sample loses 55,763% of its total mass when heated to 800^{0}C. The differential thermal curve of the studied substance is represented by one endothermic peak and one exothermic peak. The first endothermic reaction occurs at 36,72-115,76^{0}C, which is explained by the loss of hygroscopic and crystallization water from the substance. Exothermic peaks are observed at 392,71-504,57^{0}C, and in these intervals, it is due to the release of water as a result of mutual polycondensation of active groups in the substance -OH, -SO_2OH. We can observe that the destruction of the substance occurs at a temperature above 600^{0}C. For cationite KU-2, an endothermic peak with energy absorption is observed at 353-413 K, and its destruction is observed at 423 K. Thus, it was found that the thermal stability of the obtained polymethyleneanthracene sulfoacid based on anthracene is higher than the imported KU-2 cationite [128; pp. 131-137, 129; pp. 59-63, 130; pp. 8-13, 131; 100-110 pp.].

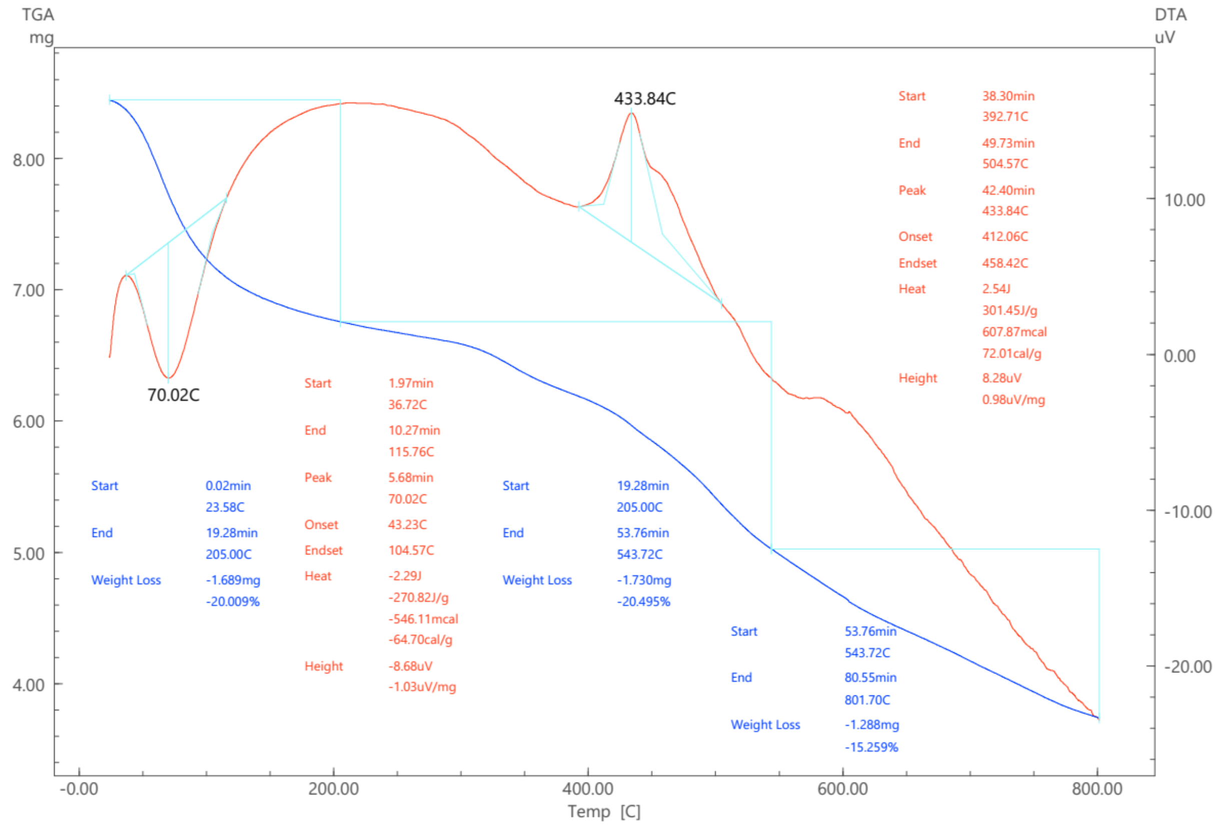


Figure 7. TG of SOF-2 - thermogravimetric curve; DSC is a differential scanning calorimetry curve

Conclusion. In order to study the composition of the secondary product of pyrolysis of hydrocarbons, the liquid part was first separated by vacuum extraction. The composition of the fractions at 200-220^{0}C and 320-360^{0}C was analyzed by chromato-mass spectrum. The physical properties of co-products and residues that were not plowed were studied.

Anthracene sulfoacids were synthesized by sulfonation of anthracene isolated from tar-product. The influence of temperature, duration of reaction, molar ratio of reagents and concentration of acid on the course of the process was studied, and optimal conditions for the synthesis of 1-anthracene sulfoacid were following: molar ratio of anthracene and concentrated sulfuric acid (93%) 1:1.2, temperature 160^{0}C and duration of reaction 6 hours. The product yield is 82%.

Based on the synthesized anthracene sulfoacids, the optimal conditions for the synthesis of spatially structured polymethyleneanthracene sulfoacid were determined. The structure, composition and properties of the synthesized substances were determined using IR-spectroscopy, chromo-mass spectrometry, SEM and thermogravimetric methods.

COE = 0,80 g/cm^3, Vs = 5 cm^3/g of spatially structured polymethyleneanthracene sulfoacid (SOF-1) obtained by polycondensation of 1-anthracene sulfoacid with formaldehyde in a 1:1.6 mol ratio at 100-110^{0}C temperature and pressure for 5 hours was determined .

COE = 1,044 g/cm^3, Vs = 4,6 cm^3/g of spatially structured polymethyleneanthracene sulfoacid (SOF-2) obtained as a result of polycondensation at 100-110^{0}C temperature and pressure for 4 hours in a 1:2 mole ratio of anthracene sulfoacids and formaldehyde was determined.

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