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STUDY OF THE SYNTHESIS AND STRUCTURE OF POLYETHYLENE NAPHTHALENE CARBONIC ACID

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Abstract

The article presents the research results of synthesizing weakly acidic polycondensation type catio-nites based on naphthalene homologs isolated from local raw materials and studying their structure using various physicochemical analysis methods. Pyrolysis oil, a secondary product of the pyrolysis process of JV "Uz-Kor Gas Chemical" LLC, was selected for the research, and naphthalene homologs were separated from its composition by fractionation and used as raw materials in further work. During the polycondensation of naphthalene carbonic acid with formalin, polymethylene naphthalene carbonic acid was obtained in the process of obtaining a weak cationic, and its composition was compared using SEM (scanning electron microscope), IR-spectrum, TG (thermogravimetry) and DTA (differential thermal analysis).

Keywords. *Naphthalene homologs, synthesis, SEM, IR, TG, DTA, naphthalene carbonic acid, formalin, catalyst, zinc chloride, polycondensation*

Introduction

Pyrolysis oil is a secondary product of pyrolysis, the composition of which depends on the raw material, and consists of a mixture of hydrocarbons with a boiling point above 180 °C. Currently, pyrolysis products do not have a specific field of use, but in most cases, they are used as a component of steam boiler fuel. Secondary products of pyrolysis reach 325.000 tons per year in Russia. The volume of production at the Naftan plant of Belarussian "Polymir" OJSC is 12.000–16.000 tons per year. As a result of the analysis of the results of chromatography of the composition of the liquid concentrate by Belarusian scientists, it was found that it contains more than 225 individual substances. They contain 67% by weight of aromatic hydrocarbons, particularly naphthalene, and their homologs up to 18% (Prech E., Byul'mann F., Affol'ter K., 2006; Turnbull L., Liggat J.J., Mac Donald W.A., 2013; Guoqiang Wang, Guitang Yang, Min. Jiang, Rui. Wang, Yin Liang, Guangyuan Zhou, 2021; Roupakias C.P., Bikiaris D.N., Karayannidis G.P., 2005; Jeong Y.G., Jo W.H., Lee S.C., 2002; Stier U., Schawaller D., Oppermann W., 2001; Lorenzetti C., Finelli L., Lotti N., Vannini M., Gazzano M., Berti C., Munari A., 2005.

Synthetic ion exchangers are produced in industry in two ways:

– polymerization or polycondensation of initial monomer compounds whose molecules have active groups;

– by introducing functional groups into macromolecules obtained from the copolymerization of vinyl aromatic compounds with dienes.

The first method is more practical because the production of ignites by chemical modification of polymers is associated with the following difficulties: multi-stage, labor intensive, the need to use toxic products, and partial decomposition of macromolecules (Bellami, L., 1971; Nakanisi, K., 1963; Chung, T.C., 2002; Hustad, P.D.; Coates, G.W., 2002; Charlesby, A., 1960; Chapiro, A., 1962; Coqueret, X., 2008.

Table 1. *Raw material composition and properties of some cations*

Brand	COE0.1 n. NaOH mg-eq/g	Comparison size ml/g	Active functional group	The main raw material
Carboxyl cations based on polymerization				
КМ	7.4–7.6	–	‹COOH	Methacrylic acid, DVB
НМД	7.8–8.8	–	‹COOH	Methacrylic acid, DVB
КМТ КМДА КМТБ	10.1 (0.4)	3.5	‹COOH	Methacrylic acid, acrylamide
КР	7.7	–	‹COOH	Methacrylic acid, DVB
КU-2–8	5.1	2.8	$-SO_3H$	Stirol, DVB
Sulcocations based on polycondensation				
КУ-1	4.2–4.7 (2.0–2.5)	2.7–3.0	‹OH	Phenolsulfoacid, formaldehyde
КУ-6	5.5 (3.4)	2.7	‹COOH	Anthracene, formaldehyde
СН	6.5 (3.9)	3.0	‹OH	Phenolformaldehyde resin, novalak
ССФ	3.9–4.0	3.7	‹OH	Sterol, formaldehyde
Polikondensatlash asosidagi fosfokationitlar				
РФ	5.0	–	$‹PO_3H_2$, ‹OH	Phenol, resorcinol, formaldehyde
ВФ	4.5	3.0–3.5	$‹PO_4H_2$	Polyvinyl alcohol
АР	3.0	1.5–1.6	$‹AsO_3H_2$, ‹OH	Oxyphenylcresol acid, formalin

Ionites contain active (ionogenic) groups (derived from the Greek word “geneticos,” meaning “to give birth”). Synthetic ion exchangers are divided into three main groups:

– Cation exchangers;

– Anion exchangers;

– Amphoteric ion exchangers (polyampholytes).

Cation exchangers are polymers that possess acidic properties and can absorb positively charged ions (cations) from electrolyte solutions.

Anion exchangers are polymers that exhibit the ability to absorb negatively charged ions (anions) from solutions and exchange them for other anions. They display basic properties.

Amphoteric ion exchangers are called polyampholytes, and they contain acidic and basic ionogenic groups. Depending on the conditions, both cation and anion exchangers can exhibit these properties.

The purpose of the work: synthesis of monomers (ethylene and propylene) for the polymer production process at “Uz-Kor Gas Chemical” LLC, a secondary product of pyrolysis device, deep processing of pyrolysis oil, separation of naphthalene homologs, the study of the synthesis process of polymeth-

ylenenaphthalene carboxylic acid mixture, based on them is to create technology for production of acidic cationic and special additives for concrete mixtures.

Table 2. *Active groups in ionites*

Cationite		Anionite	
Available ion	Counter ion	Available ion	Counter ion
SO_3^-	H^+	$-NH_3^+$	OH^-
COO^-	H^+	$=NH_2^+$	OH^-
PO_3^{-2}	H^+	$\equiv NH^+$	OH^-
SeO_3^-	H^+	$==N^+$	OH^-
AsO_3^{-2}	H^+		

Materials and methods

To extract naphthalene and its homologs from the composition of pyrolysis oil, the secondary product "pyrolysis oil" from the Ustyurt gas-chemical complex, which belongs to "Uz-Kor Gas Chemical" LLC, was used as a raw material.

Chromatomass-spectrum results showed that natalin and its homologs constitute the main part of pyrolysis oil. Among these products, naphthalene homologs make up 28.34% of the total.

Pyrolysis oil was divided into fractions using rectification drive, and their composition was studied (Table 1). 1-methylnaphthalene and 2-methylnaphthalenes account for up to 80% of the fraction between 220–250 °C, while 1,6-dimethylnaphthalene accounts for up to 48% of the fraction at 260–270 °C.

The sodium and calcium salts of polymethylenenaphthalene carboxylic acid (PMNK), which is the focus of the research, serve as highly effective diluents with a high molecular fraction content. However, the synthesized polycondensate contains free formaldehyde, which negatively affects the ecological characteristics of the finished product.

The technological process of producing polymethylenenaphthalene carboxylic acids (PMNK) consists of the following stages:

– Oxidation of 2-methylnaphthalene with concentrated nitric acid to obtain β-naphthalene carboxylic acid.

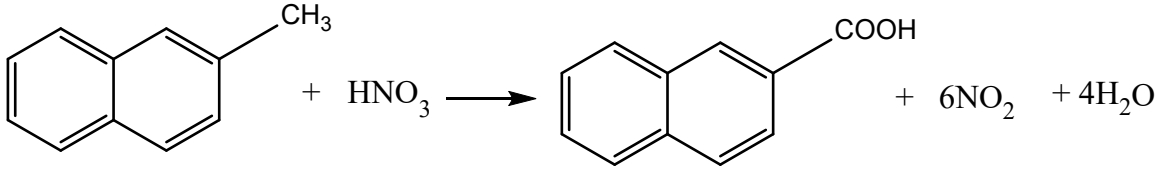
– Polycondensation of β-naphthalene carboxylic acid with formaldehyde to obtain polymethylenenaphthalene carboxylic acid.

– Neutralization of the resulting reaction product with sodium hydroxide or calcium hydroxide.

– Filtration of the additive solution to remove sodium/calcium deposits.

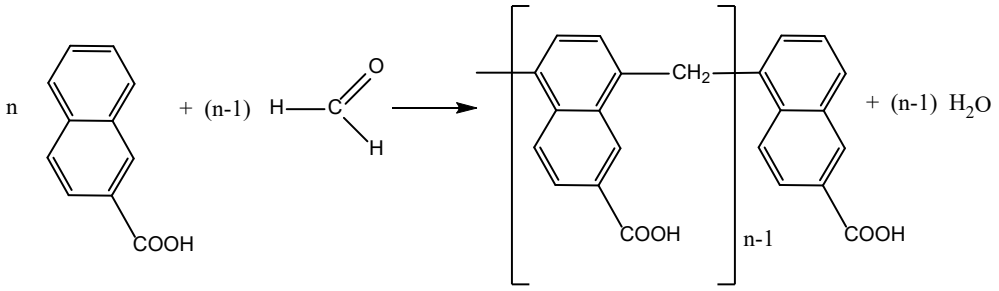
Depending on the conditions of the process, substances with different properties are formed. We analyze all stages of the technological process.

At the stage of oxidation of 2-methylnaphthalene with concentrated nitric acid, the production of β-naphthalene carboxylic acid is the main process.



Depending on the temperature of the oxidation process, a mixture of different naphthalic acids is formed. Therefore, the oxidation process is carried out at a temperature higher than 120 °C. When the temperature rises above 150 °C, the level of side processes increases, resulting in an increased amount of various acids. Conversely, decreasing the temperature of the process below 120 °C leads to an increase in the amount of other oxygenated organic compounds that do not oxidize into 2-methylnaphthalene acid.

The polycondensation reaction of naphthalene carboxylic acids with formalin proceeds according to the following scheme:

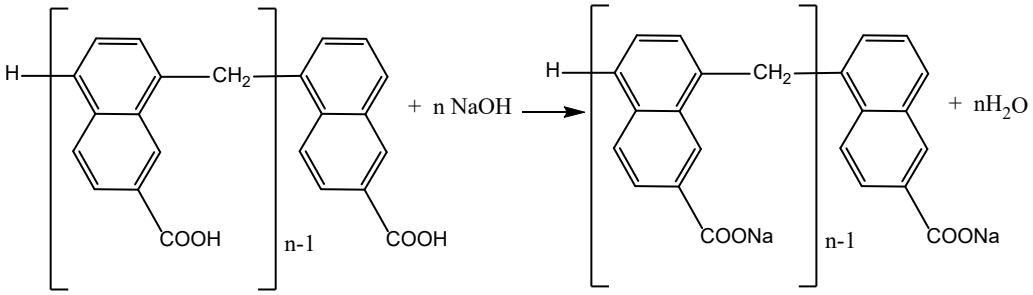


The polycondensation process is carried out at a temperature of 110 °C for several days. The longer the process continues, the higher the content of the polymerized substance in the product, as well as the higher the content of the active substance. The completion of the process is monitored through sampling. When cooled, the resulting polycondensate transforms into a viscous mass. When stretched, it forms thin fibers and dissolves in water.

To reduce the time and energy consumption of the polycondensation process, the reaction was carried out at high temperature and high pressure in a special setup, allowing the reaction to be completed within a few hours. Formalin is introduced into the reaction mixture from multiple points and below the reaction mass to ensure uniform distribution throughout. If formalin is added from a single point, it can increase the viscosity of the reaction mass, potentially leading to issues such as mixer failure and other complications.

During the neutralization stage of the polycondensation process, the sodium salts of polymethylenenaphthalene carboxylic acid are formed by treating the condensed mass with sodium hydroxide. The condensed mass is mixed with a specific amount of water and then diluted and cooled. Next, an alkali solution is added, and the mixture is stirred until the medium becomes neutral.

The reaction equation for the neutralization process is as follows:



During the synthesis of the additive, the residual formaldehyde mass fraction of 0.001% remains higher than usual, which cannot be used in the composition of construction materials used for the interior decoration of buildings with a lot of people.

To reduce the mass fraction of residual formaldehyde in the production process of the additive, they proposed to use the Cannizzaro reaction. Formaldehyde molecules interact and turn into various harmless organic substances. In such a process, a disproportionation reaction occurs, one molecule of formaldehyde is reduced and the second molecule is oxidized, alkalis play the main role as a catalyst of the process (Bellami L. 1971):

$$2CH_2O + H_2O = CH_3OH + HCOOH$$

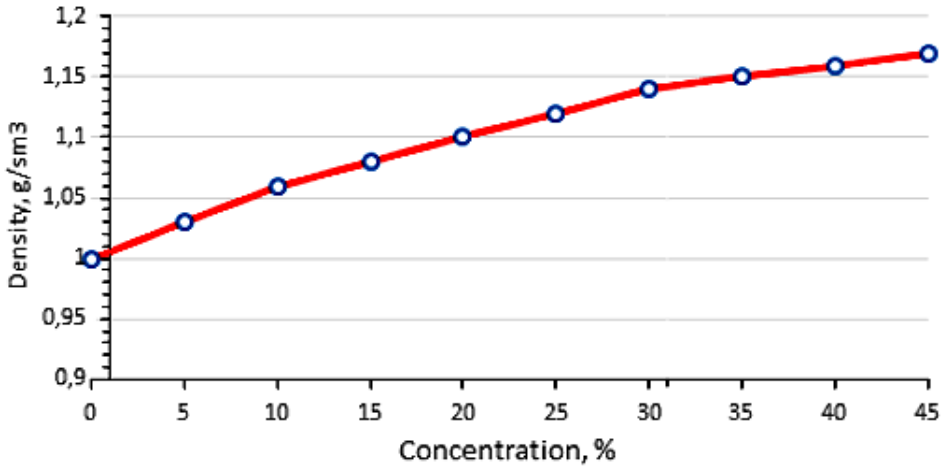
Aldehydes without a hydrogen atom in the alpha state undergo disproportionation under the influence of concentrated alkali solutions to form carbonic acid and alcohol.

The mechanism of the Cannizzaro reaction combines a two-stage nucleophilic addition reaction: in the first stage, the hydroxyl anion is attached to the carbonyl group of the formaldehyde molecule, then hydrogen is released from this adduct compound in the form of a hydride-anion and combines with the second molecule of formaldehyde. For example, formaldehyde is converted into methyl alcohol with potassium formate (since there is potassium hydroxide in the environment).

The Cannizzaro reaction was carried out at a high temperature of 100 °C for several hours. After the process was completed, the product was neutralized with a low-concentration sulfuric acid solution. As a result, the mass fraction of formaldehyde in the liquid product of the process did not exceed 0.001%.

To evaluate the transportability of the synthesized additive solution, the relationship between its concentration and density was determined. The results of the experiments are presented graphically in Figure 1. One of the most important characteristics of the diluent-plasticizer, which affects the gypsum mixture, determined by the Suttard method, is the plasticity index (Orifjon Kadyrov, Zilola Karimova, 2023).

Figure 1. *Graph of dependence of additive density on solution concentration*



To synthesize polymethylenenaphthalene carboxylic acid (cationic) with a spatial structure, the following successive works were carried out;

– Naphthalene homologs were isolated from pyrolysis oil.

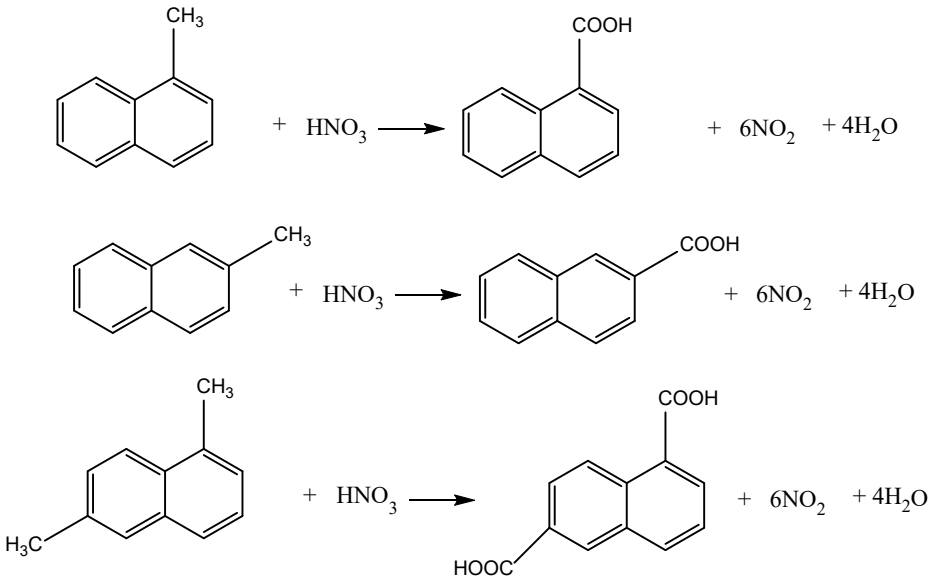
– Obtained naphthalene homologs were oxidized and naphthalene carboxylic acids were synthesized. (I-reaction)

– Naphthalene polycondensates a mixture of carboxylic acids with formalin (1 : 2 molar ratio of carboxylic acids and formaldehyde) under high pressure, and the polycondensate is heated at 95 – 100 °C for 24 hours.

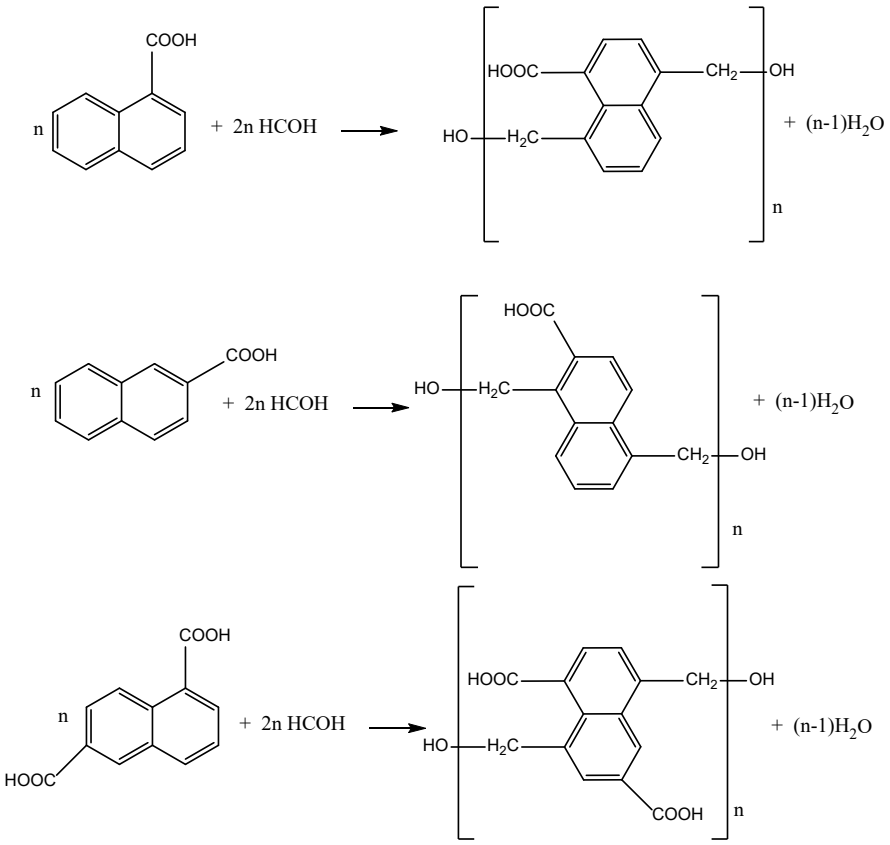
(Reactions II and III)

The reaction equation of the above processes is as follows:

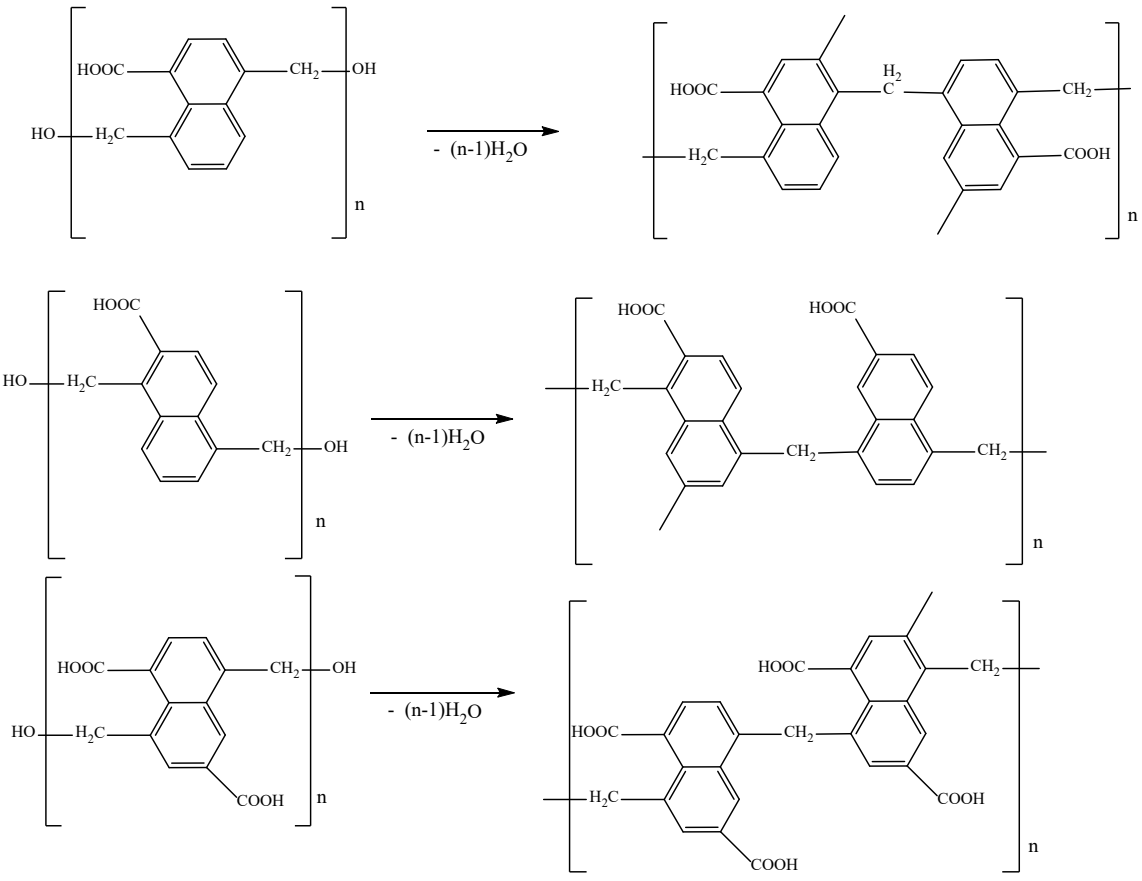
I-reaction



II-reaction



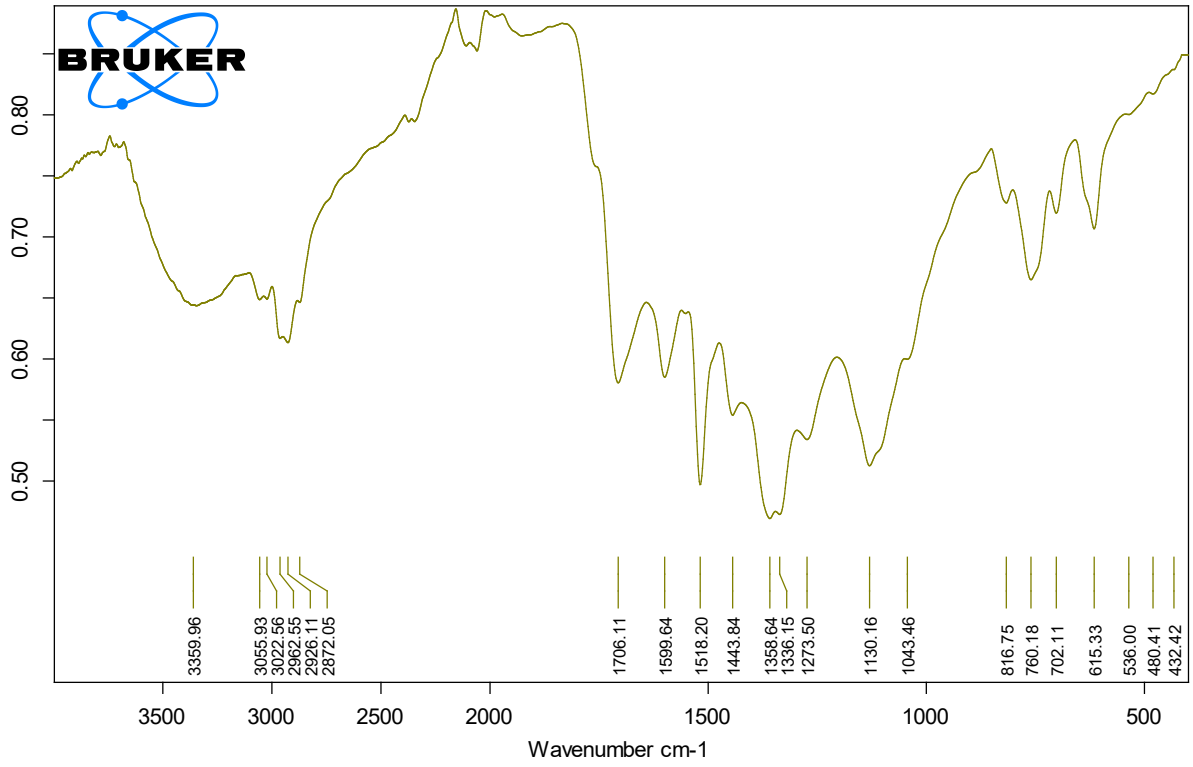
III-reaction



Results and discussion

The IR spectrum of synthesized 1-naphthalene carboxylic acid was obtained and analyzed.

Figure 2. *IR spectrum of 1-naphthalene carboxylic acid*



The analysis of the above IR spectrum shows that. We can see the valence vibration of the –OH group at 3359.96 sm^{-1}, the valence vibration of the C-H bond in the aromatic core at 3055.93 sm^{1}, and the valence vibration of the $–CO_2H$ group at 1130.16 sm^{-1}. The element analysis of the synthesized polymethylenenaphthalene carboxylic acid with spatial structure was performed (Figure 3).

Figure 3. *Elemental analysis of polymethylenenaphthalene carboxylic acid with spatial structure*

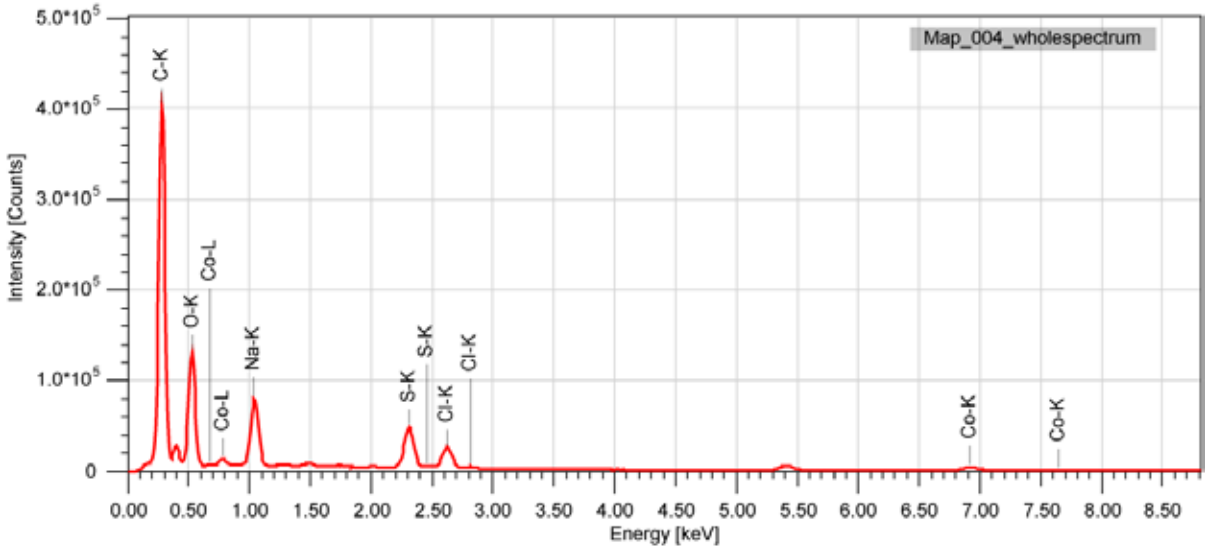
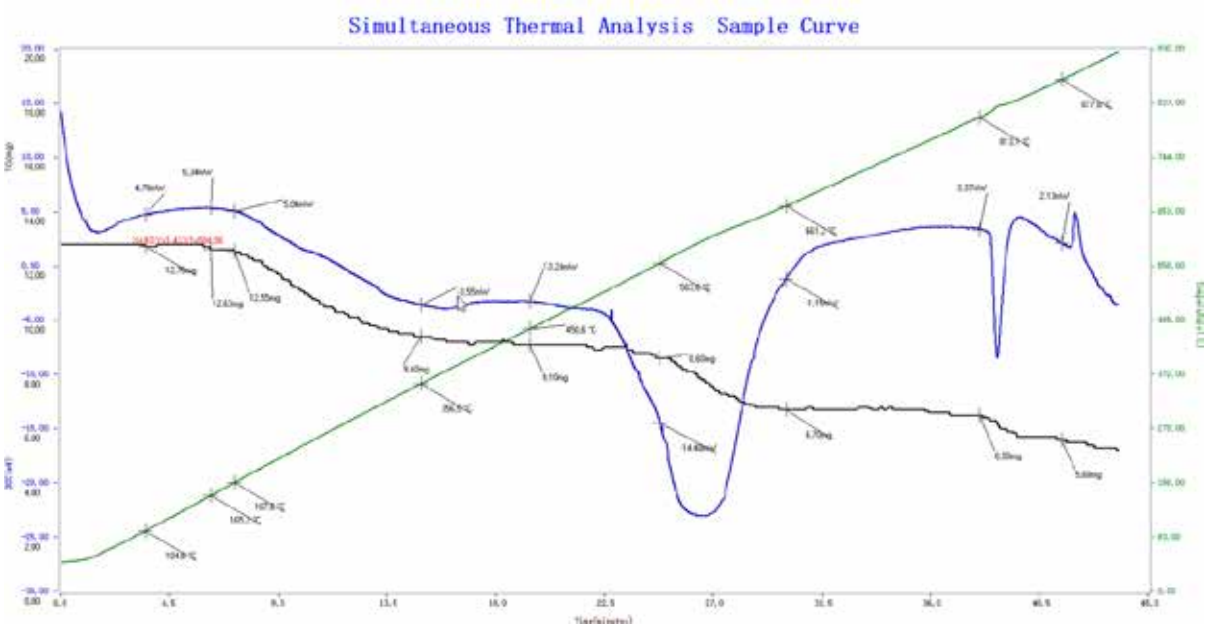


Table 3. *Results of elemental analysis of polymethylenenaphthalene carboxylic acid with spatial structure*

Element	Mass fraction (%)	A fraction of the atomic number (%)
C	62.55	71.32
O	28.3	24.22
Na	4.65	2.77
S	2.25	0.96
Cl	1.3	0.5
Co	0.96	0.22

Figure 4. *TG of carbocationite – thermogravimetric curve; DTA – differential thermal curve*



Thermal stability of carbocationite was studied by the thermogravimetric method

The data presented in the figure shows the change in sample composition with weight loss. The first stage, in the temperature range of 104.6–356.5 °C, exhibits a weight loss of 26.27%. The second stage, ranging from 450.6–661.2 °C, shows a weight loss of 21.12%. Additionally, in the temperature range of 813.1–877.8 °C, a substance mass loss of 8.63% was observed. Overall, the resulting carbocationite experienced a total mass loss of 56.07% when heated to 900 °C.

The differential thermal curve of the studied cationites shows two endothermic peaks. These endothermic effects can be attributed to the thermal degradation of the cationite, occurring in the ranges of 450.6–661.2 °C and 813.1–877.8 °C.

In the case of the KU-2 cationite, an endothermic peak with energy absorption is observed at 353–413 K, and its degradation is observed at 423 K [24–26]. This indicates that the thermal stability of the naphthalene-based cationite is higher compared to that of the KU-2 cationite.

The following operational properties of carbocationic were studied:

- specific mass of cationic
- the specific volume of the cation
- wettability of the cation
- static exchange capacity of cationic
- dynamic exchange capacity of cationic

Work was carried out according to the GOST 10896–78 international standard to prepare the received catonites for testing. For comparison, sulfocationite KU-2–8 was obtained (Table 4).

Table 4. *Synthesized carbocationic and KU-2–8(imported) sulfocationite operational properties*

№	A type of cationite / Learning method	Comparative mass (g/dm³) GOST 10898.2–74	Humidity (%) vlagamer XY-100MW	Comparison size (sm³/g) GOST 10898.4–84	Total static capacitance (mg-eq/g) GOST 20255.1––89	Dynamic exchange capacity (mol/m³) GOST 20255.2–89
1	NKK	765	54.7	4.7	4.92	512
2	KU-2–8 (control)	750–800	48–58	2.8	4.6–4.8	500–520

It can be seen from the table that the main performance properties of the synthesized NKK carbocationites are close to the static and dynamic exchangeability of imported sulphocationite KU-2–8.

Summary

Polymethylenenaphthalene carboxylic acids were obtained based on naphthalene obtained from pyrolysis oil, a secondary product of the hydrocarbon pyrolysis process, and it was found that the linear oligomer of this polymer can be used as a superplasticizer in concrete mixtures, and its spatial polymer can be used as a carbocationic.

Chromato-mass spectrum, IR spectrum, SEM analysis, elemental analysis, and TG analysis were used to study and analyze the composition, structure, and properties of the products obtained as a result of the synthesis.

The use of synthesized oligomers with a linear structure as a superplasticizer in concrete mixtures has been studied to increase the plasticity and strength of the intermediate mixture.

The cationic property of the synthesized polymethylenenaphthalene carbonic acid was studied, and it was put into practice as a cationic in the purification of circulating water in factories from various metal cations.

COE (static exchange capacity) and DOE (dynamic exchange capacity) were determined as important operational properties of cation sites. COE = 4.92 mg-eq/g, DOE = = 512 mol/m³. The static and dynamic exchange capacity of the synthesized carbocationites was studied to be close to the property of KU-2–8 sulfocationite.

The thermal stability of carbocationite was studied by the thermogravimetric method. It was found that the thermal stability of the obtained cationite based on naphthalene is higher than that of KU-2 cationite.

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