European Science Methodical Journal
ISSN (E): 2938-3641
Volume 3, Issue 5, May- 2025

SYNTHESIS OF CATION EXCHANGERS USED FOR WASTEWATER TREATMENT FROM METHYLNAPHTHALENE

F. Sh. Boboqulova,
Associate Professor of the Faculty of Food Engineering,
Shahrisabz Branch, Qarshi State Technical University
firuzaboboqulova87@gmail.com

N. Raxmatova,
Master's Degree Student at the Faculty of Food Engineering,
Shahrisabz Branch, Qarshi State Technical University

Abstract:

This article investigates the process of separating naphthalene homologs from pyrolysis oil. The composition of the pyrolysis oil was analyzed using chromatographic methods, and optimal conditions for separation were determined. The oxidation processes of naphthalene homologs to synthesize naphthalene carboxylic acid were studied. The oxidation kinetics of naphthalene homologs and the composition of the resulting products were examined using infrared spectroscopy (IR), thermogravimetric analysis (TG), and chromatographic techniques. These findings are highly valuable for the application of naphthalene derivatives in organic synthesis.

Keywords: Pyrolysis oil, naphthalene homologs, oxidation, catalysis, infrared spectroscopy, thermogravimetry, fractional separation, chromatography, naphthalene carboxylic acid, polycondensation, polymethylenenaphthalene carboxylic acid, extraction.

Introduction

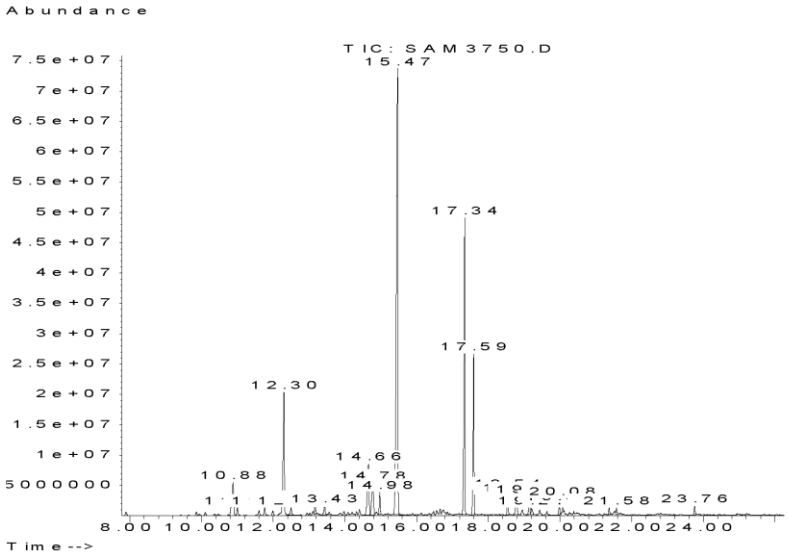
Pyrolysis oil is a complex mixture formed during the pyrolysis of hydrocarbons, containing various aromatic hydrocarbons, including naphthalene and its homologs. The extraction of these components and the development of efficient utilization methods hold significant scientific and industrial importance. Naphthalene and its homologs are widely used organic compounds in the chemical industry. The oxidation of these compounds yields naphthalene carboxylic acids, which find applications in pharmaceuticals, polymers, and dye manufacturing. This study explores the oxidation processes of naphthalene homologs extracted from pyrolysis oil to synthesize their corresponding carboxylic acids. The potential for producing high-molecular-weight polymers through polycondensation reactions of naphthalene carboxylic acid has become a pressing topic in modern polymer chemistry. This article analyzes

European Science Methodical Journal
ISSN (E): 2938-3641
Volume 3, Issue 5, May- 2025

the synthesis process of polymethylenenaphthalene carboxylic acid via the polycondensation of naphthalene carboxylic acids in the presence of formalin.

Materials and Methods

Pyrolysis oil is an oily liquid with an unpleasant odor, ranging in color from dark brown to dark green. Its composition is unstable and depends on the feedstock used in the pyrolysis process. To qualitatively and quantitatively analyze the chemical composition of pyrolysis oil, a secondary by-product from the production at “Uz-Kor Gas Chemical” LLC JV was used. The analysis was performed using an Agilent 5977A gas chromatograph equipped with a mass-selective detector. The prepared sample was analyzed using an Agilent Technology GS 6890/MS 5973N gas chromatograph-mass spectrometer with a 30 m × 0.25 mm capillary column coated with 5% phenylmethylsiloxane in dimethylsiloxane. The carrier gas was hydrogen, injector temperature was 280°C, MS source temperature was 230°C, MS quadrupole temperature was 180°C, and the column oven temperature program ranged from 100°C to 280°C with a heating rate of 10°C/min. The sample volume was 1 µL in splitless mode. The results obtained are presented in Figure 1 and Table 1.



1. – Figure. Chromatogram of pyrolysis oil.

Physical Properties of Pyrolysis Oil

Property	Value
Density at 20°C (g/cm³)	0.9578
Kinematic viscosity at 20°C (mm²/s)	38
Coking tendency (%)	14
Water content (%)	0.3
Mechanical impurities (%)	0.01
Evaporation temperature (°C)	180

European Science Methodical Journal
ISSN (E): 2938-3641
Volume 3, Issue 5, May- 2025

Table 1. Chemical Composition of Pyrolysis Oil, a Secondary By-Product of Production at "Uz-Kor Gas Chemical" LLC JV, Based on Qualitative and Quantitative Analysis Results

№	Substance	Amount, %	Conformance with Base Data, %
1	Indene	9.33	93
2	1-Methylindene	8.96	96
3	Naphthalene	41.51	90
4	1-Methylnaphthalene	8.61	97
5	2-Methylnaphthalene	16.25	96
6	1-Ethylnaphthalene	1.77	90
7	1,6-Dimethylnaphthalene	1.71	95

The main stages in the separation of naphthalene homologs are as follows:

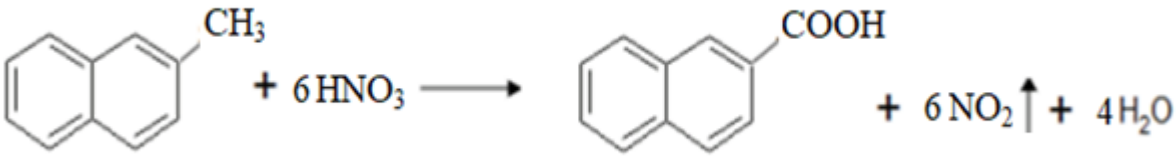
- **Analysis of pyrolysis oil:** The compositional components were identified using gas chromatography–mass spectrometry (GC-MS).
- **Fractional separation:** Pyrolysis oil was separated into different temperature ranges by means of fractional distillation.
- **Extraction:** Naphthalene homologs were isolated and purified using organic solvents.

Fractional Composition of Pyrolysis Oil

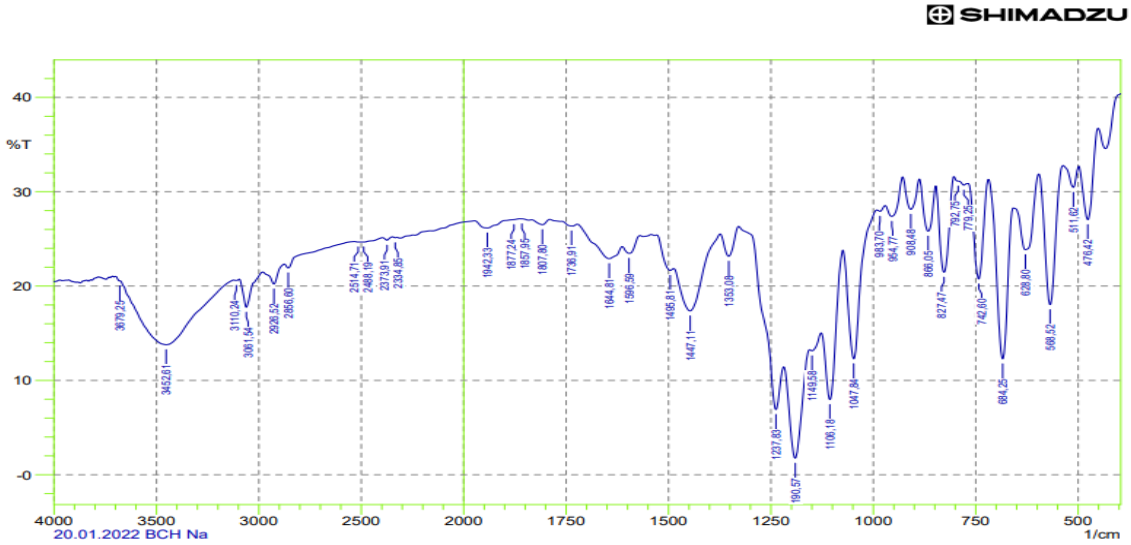
Fr. No.	Temperature Range (°C)	Main Components in the Fraction	Mass Fraction of the Product (%)	Mass Fraction of the Fraction (%)
1	185–210	Indene, 1-Methylindene, Tetralin	70.0	16.85
2	210–220	Naphthalene	92.0	32.9
3	220–235	Naphthalene, 1-Methylnaphthalene, 2-Methylnaphthalene	85.0	22.4
4	235–250	1-Methylnaphthalene, 2-Methylnaphthalene	88.0	10.3
5	250–260	Diphenyl	21.0	2.3
6	260–270	1,6-Dimethylnaphthalene	40.1	1.8
7	270–280	Acenaphthene	50.0	1.2
8	280–290	Trimethylnaphthalene	75.0	1.95
9	290–300	Fluorene	52.0	1.2
10	–	Residue	–	7.5

The main process in the oxidation of 2-methylnaphthalene using concentrated nitric acid is the formation of β-naphthalene carboxylic acid.

European Science Methodical Journal
ISSN (E): 2938-3641
Volume 3, Issue 5, May- 2025



Depending on the oxidation temperature, a mixture of different naphthalene acids is formed. Therefore, the oxidation process is carried out at temperatures above 120°C. When the temperature exceeds 150°C, the rate of side reactions increases, leading to the opening of the aromatic ring and an increase in the amount of various acids. If the temperature drops below 120°C, 2-methylnaphthalene does not fully oxidize to the acid, and the amount of other oxygen-containing organic compounds increases.The IR spectrum of the naphthalene carboxylic acid obtained from the oxidation of methylnaphthalene was recorded and analyzed.

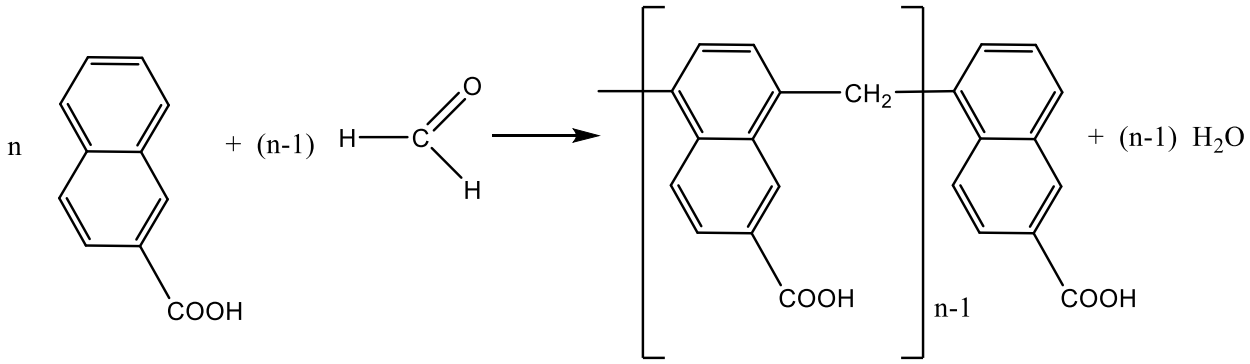


3-image. IR Spectrum of Naphthalene Carbon Acid.

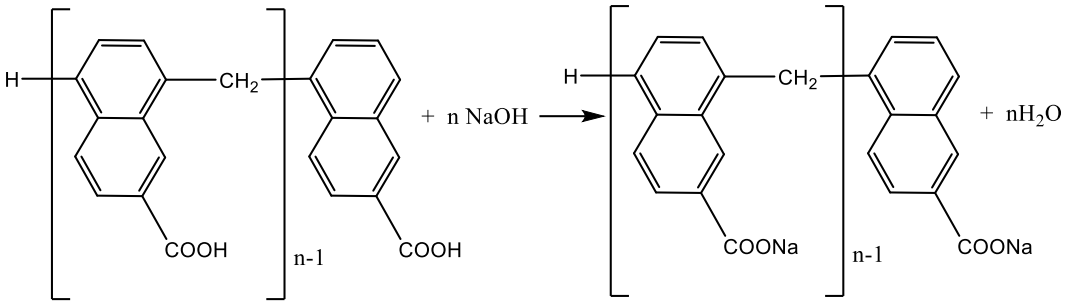
The polycondensation process of naphthalene carboxylic acid involves the following steps: Preparation of reagents: Naphthalene carboxylic acid and a 35% formalin solution were prepared. The polycondensation was performed at 110°C over an extended period. The longer the process lasts, the higher the degree of polymerization in the product, which results in an increase in the amount of active substances in the product. Process completion was tracked by periodic sampling and analytical assessment. After cooling, the obtained polycondensate turns into a viscous mass, which, when stretched, forms a thin fiber and dissolves in water.

European Science Methodical Journal
ISSN (E): 2938-3641
Volume 3, Issue 5, May- 2025

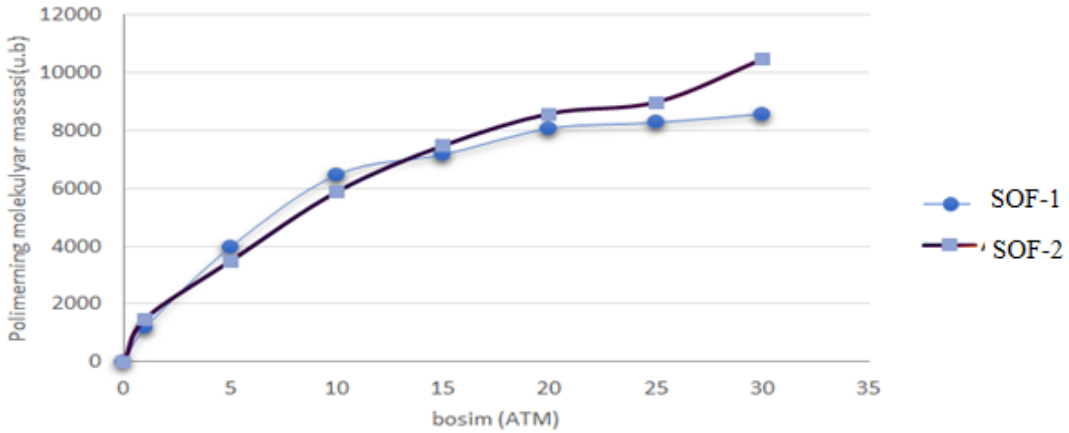
Polycondensation reaction equation:



During the neutralization stage of the polycondensation process with sodium hydroxide, sodium salts of polymethylenenaphthalene carboxylic acid are formed. A certain amount of water is added to the condensed mass to dilute it, then it is cooled, and an alkaline solution is added. The sodium hydroxide solution is mixed until the environment becomes neutral.



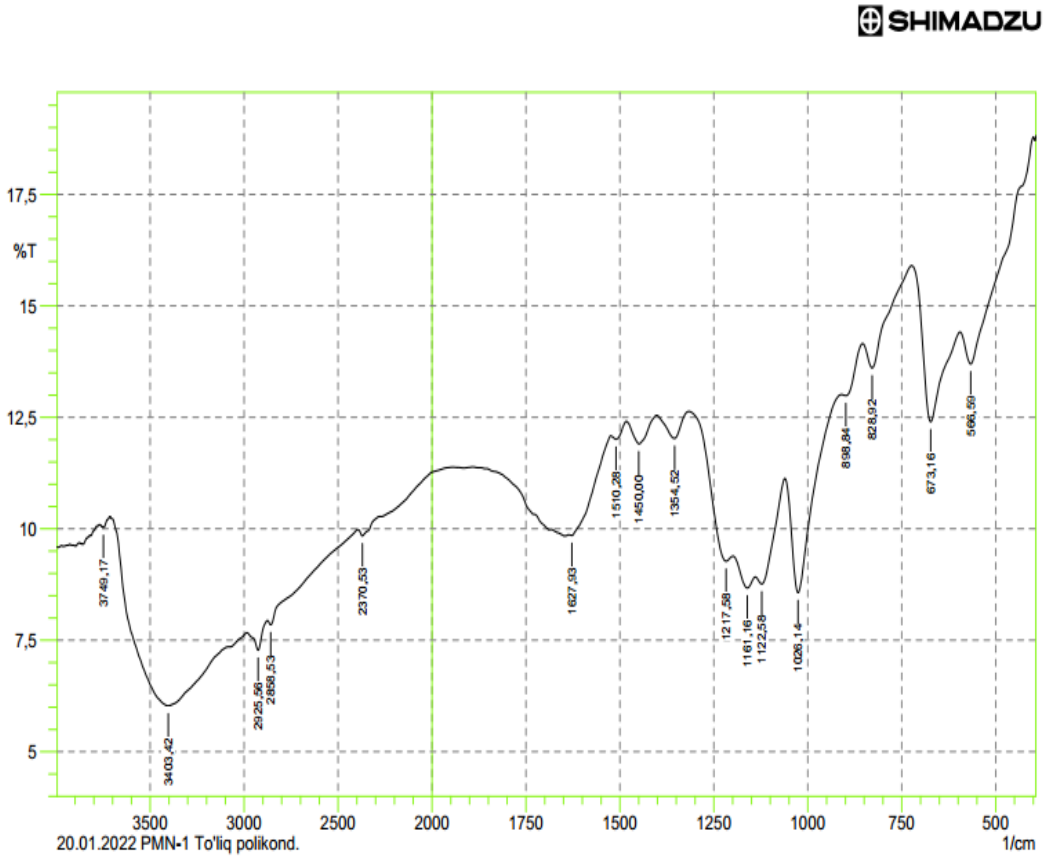
In the polycondensation process, an increase in pressure contributes to a higher molecular mass of the obtained phase polymer. The graph in the image shows the relationship between polymer molecular mass and pressure.



4-image The relationship between the molecular mass of SOF-1 and SOF-2 polymethylenenaphthalene carboxylic acids and pressure.

5-image The IR spectrum of polymethylenenaphthalene carboxylic acid

European Science Methodical Journal
ISSN (E): 2938-3641
Volume 3, Issue 5, May- 2025



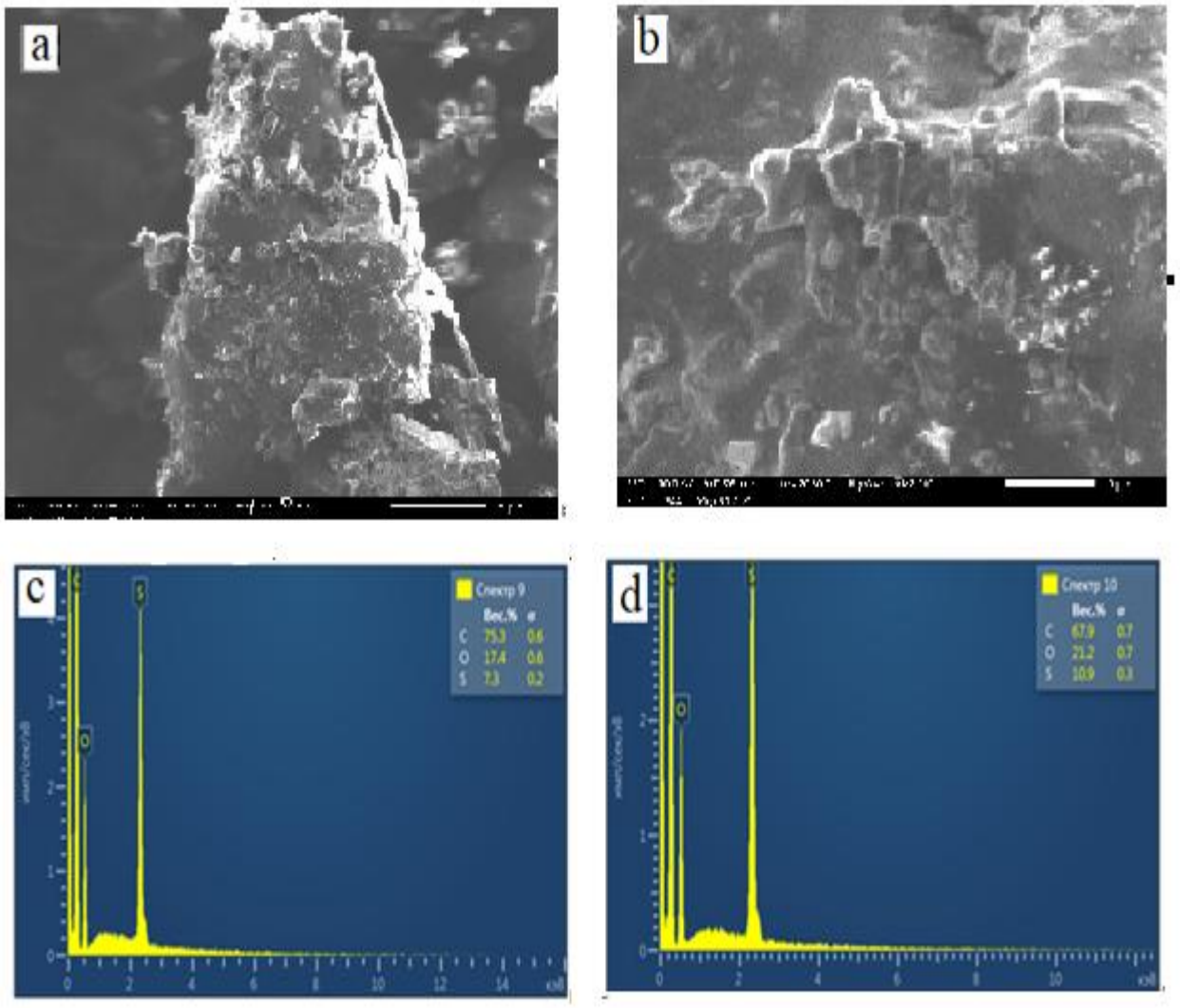
6-image The IR spectrum of polymethylenenaphthalene dicarboxylic acid

The synthesized polymethylenenaphthalene carboxylic acid and polymethylenenaphthalene dicarboxylic acid were analyzed using SEM (scanning electron microscopy) to determine the morphology, surface structure, and elemental composition of phase-structured polymethylenenaphthalene carboxylic acids.

The SEM analysis results of polymethylenenaphthalene carboxylic acid are presented in Figures 7-(a,c). The SEM results show that it contains macropores ranging from 97 μm to 340 μm in size.

The SEM analysis results of polymethylenenaphthalene dicarboxylic acid are presented in Figures 7-(b,d). According to the analysis, it contains macropores ranging from 114 μm to 613 μm. It is known that macroporous cation-exchange resins exhibit high mechanical strength and osmotic stability. SOF-2 has higher mechanical strength compared to SOF-1. Based on elemental analysis, SOF-1 contains less oxygen than SOF-2. Therefore, SOF-2 has a higher amount of –COOH. As a result, the COE and DOE properties of SOF-2 are also higher than those of SOF-1.

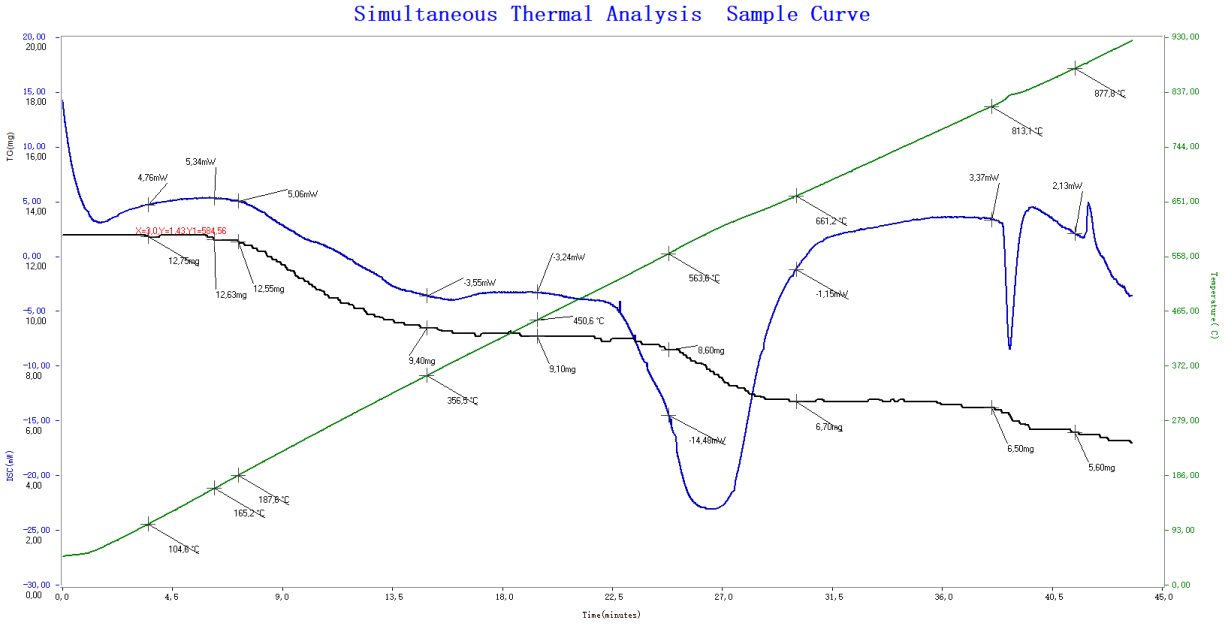
European Science Methodical Journal
ISSN (E): 2938-3641
Volume 3, Issue 5, May- 2025



7-image. a,c - SOF-1, b,d - SOF-2 larning sirt tuzilishi va element tarkibi.

The thermal stability of the synthesized polycondensate products was studied using thermogravimetric (TGA) analysis. The data presented in Figure 4.1.8 show the changes in the sample structure with mass loss in three stages: the first stage, between 27.01–152.07°C, shows a mass loss of up to 22.989%; the second stage, between 152.07–369.56°C, shows a mass loss of 22.065%; and from 369.56–900.9°C, a further 22.554% mass loss occurs. It was determined that when heated up to 900°C, the total mass loss is 67.608%. The differential thermal curve of the studied substance is characterized by two endothermic peaks and two exothermic peaks. The first endothermic effect occurs at 41.14–94.52°C, which is explained by the loss of hygroscopic and crystallization water from the substance. The second endothermic peak appears at temperatures above 600°C and is attributed to the destruction of the substance.

European Science Methodical Journal
ISSN (E): 2938-3641
Volume 3, Issue 5, May- 2025



8-image The TG - thermogravimetric curve of the weak cation-exchanger

The pyrolysis of hydrocarbons was studied, and the secondary product, "pyrolysis oil," was analyzed using chromatographic-mass spectrometry. It was found to contain a significant amount of naphthalene and its homologs. As a result, the naphthalene homologs were separated and purified through fractional distillation.

- Oxidation of naphthalene homologs led to the synthesis of mono and di-naphthalene carboxylic acids (1-carboxynaphthalene, 1,6-dicarboxynaphthalene acids).
- The sodium salt of polymethylenenaphthalene carboxylic acid with a linear structure was synthesized by polycondensation of 1-carboxynaphthalene and 1,6-dicarboxynaphthalene acids with formalin in various ratios, and then it was converted to polymethylenenaphthalene carboxylic acid by washing with acid.
- Polycondensation of 1-carboxynaphthalene and 1,6-dicarboxynaphthalene acids with formalin in different ratios resulted in the synthesis of polymethylenenaphthalene carboxylic acids with a phase-structured morphology.
- The composition, structure, and properties of the obtained substances were studied and analyzed using chromatographic-mass spectrometry, IR spectroscopy, SEM analysis, elemental analysis, and TG analysis methods.

References

1. Prech, E., Bülmann, F., Affolter, K. Determination of the structure of organic compounds. Moscow: Mir, 2006.
2. Yu.A. Bulavka, V.A. Lyakhovich. Modern directions of processing heavy pyrolysis tar. NEW TECHNOLOGIES – TO THE OIL AND GAS REGION, Tyumen, 2018.

3. Chung, T.C. Synthesis of functional polyolefin copolymers with graft and block structures. Prog. Polym. Sci. 2002, 27, 39–85.
4. Walker, J.F. Formaldehyde / J.F. Walker; translated by P.P. Korzhev. Moscow: Goskhimizdat, 1957. – 608 p.
5. GOST 23789–2018. Gypsum binders. Testing methods. Replaces GOST 23789–89; effective from May 1, 2019. Moscow: Standardinform, 2018. – 11 p.
6. R.Yu. Banin, N.Ts. Gatapova. Study of the process of producing a gypsum board additive based on polymethylenenaphthalenesulfonate. Bulletin of TGTU, 2021. Vol. 27. No. 2.
7. European Standard EN 13986:2004. Wood-based panels for use in construction – Characteristics, evaluation of conformity, and marking. Text: electronic. URL: https://docplayer.net/30412682-Wood-based-panels-for-use-in-construction-characteristics-evaluation-of-conformity-and-marking.html.