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PRODUCTION OF SUPERPLASTICIZERS BASED ON THE PYROLYSIS PRODUCTS OF HEAVY RESINS

Safarov Toyir Tursunovich [1], Ziyadullaeva Kamola Xaitboevna [2], Ziyadullaev Anvar Egamberdievich [1], Eshpulatov Mukhammadi [1]

[1] Tashkent Chemical-Technological Institute of Republic of Uzbekistan, Uzbekistan

[2] University of Geological Sciences of the Republic of Uzbekistan, Uzbekistan

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Abstract

The process for obtaining naphthalene, indene, and phthalic anhydride through the distillation of liquid and solid fractions of heavy pyrolysis products has been implemented. The quantitative and qualitative composition of resin samples and the products derived from their fractions have been determined. Additionally, superplasticizer additives for cement were developed, and their strength, average particle density of the cement, the impact of the amount of superplasticizers, and their duration of action on the material properties were studied.
Keywords: pyrolytic heavy distillate, naphthalene, indene, phthalic anhydride, superplasticizer

Introduction:

The goal of pyrolysis processes, which are widely used in modern petrochemistry, is to produce lower olefins, primarily ethylene, a valuable raw material for synthesizing key petrochemical products (Pavlovich, L.B., Andreikov, E.I., 2013; Romanova, N.A., Leontyeva, V.S., Khrekina, A.S., 2018; Sahu, B.M., Bera, V.V., Kumar, R., Banik, B.K., Bora, P., 2020).

During pyrolysis, ethylene, propylene, butylene, and butadiene are generated, along with significant amounts of benzene and aromatic hydrocarbons such as toluene, xylene, indene, naphthalene, and anthracene. Ethylene obtained from pyrolysis is used to produce ethylene oxide, ethyl alcohol, polymers, styrene, plastics, and other products. The main applications of liquid pyrolysis products include the production of benzene and other aromatic hydrocarbons, oils from polymer resins, diesel fuel, coal, and high-quality coke (Sha, S., Wang, M., Cai, C., Shi, C., Xiao, Y., 2020; Ziyadullaeva, K.Kh., Nurmanov, S.E., Mukhidinov, B.F., Kodirov, O.Sh., Vapoeв, Kh.M., 2020).

To improve the quality of cement compositions, it is essential to use highly effective plasticizing additives. In the construction industry, superplasticizers — chemical additives — are employed to regulate the structural formation processes and rheological properties of concentrated suspensions, allowing for modifications in the flowability of raw materials and the properties of finished products. One of the pressing tasks today is to find new effective additives that can alter interfacial properties and rheological characteristics of dispersions (Batrakov, V.G., 1998; Gamaliy, E.A., 2009; Ibragimov, R.A., 2011; Ramachandran, V.S., 1988; Ramachandran, V.S., 1977).

Research Methods:

For the first time, catalysts of types VBS-33, VBS-44, VBS-55, and VBS-66 were created for the separation of naphthalene and indene fractions from secondary gas chemical products at various temperatures and for the production of plasticizers. The study employed methods such as UV spectroscopy, Raman spectroscopy, gas chromatography, mass spectrometry, and differential thermal analysis (DTA). Heavy pyrolysis oils from gas processing plants, naphthalene, indene and their homologues, plasticizers for concrete and cement, phthalic anhydride, and naphthalene were investigated.

Analysis of Results:

The primary direction of economic development in the Republic focuses on the development and utilization of natural resources, large-scale modernization of industrial production, technical and technological updates, the introduction of modern scientific achievements, and progressive innovative technologies in manufacturing. The creation of competitive import-substituting products with stable demand in the global market is essential.

The Ustyurt Gas Chemical Complex is one of the largest enterprises for the production of polymer products in Central Asia, based on the processing of natural gas in the Ustyurt region. The complex has an annual production capacity of 387,000 tons of polyethylene and 83,000 tons of polypropylene. More than 102,000 tons of pyrolysis distillates, 8,000 tons of pyrolysis oil, and 10,000 tons of resin are produced here. The pyrolysis distillates, pyrolysis oils, and resin products formed in this process are not currently processed. Pyrolysis distillates and oils, such as naphthalene and aromatic hydrocarbons, are now primary secondary raw materials for producing valuable chemical products essential for the industry.

The processing of heavy fractions from liquid pyrolysis products and the introduction of these products into practice are deemed relevant, allowing the production of costly and necessary products using modern technologies. Due to the lack of acceptable technologies for recycling pyrolysis waste to produce indene, naphthalene, and its homologues, phthalic anhydride is not produced in the country. Thus, research aimed at developing recycling technologies for gas chemical complex waste is a pressing issue that requires resolution.

Pyrolysis distillates, pyrolysis oil, and heavy fractions of liquid pyrolysis products are secondary raw materials with significant potential for producing naphthalene, aromatic hydrocarbons, indene, phthalic anhydride, and other valuable chemical products.

Currently, modern technologies enable the production of costly and necessary products. However, due to the absence of acceptable technologies for recycling pyrolysis waste to produce indene, naphthalene, and its homologues, phthalic anhydride is not manufactured in our country. Therefore, research aimed at developing an integrated technology for recycling waste from gas chemical complexes operating in the republic is a relevant task that needs addressing.

The process of thermal pyrolysis of hydrocarbon raw materials is the primary method for obtaining low-molecular unsaturated hydrocarbons — olefins (alkenes)—such as ethylene and propylene. The main applications of liquid pyrolysis products include the production of benzene and other aromatic hydrocarbons, naphthalene, oil polymers, gasoline, raw materials for producing high-quality coke, and more.

Currently, due to reduced oil production volumes in the petrochemical industry, the issue of expanding the raw material base for producing aromatic hydrocarbons and their various derivatives is becoming increasingly relevant. Heavy pyrolysis products, such as indene and naphthalene, along with their homologues, are of great interest as potential raw materials for producing petrochemical products.

Secondary gas chemical products were separated into naphthalene and indene fractions at various temperatures. Based on the obtained products, catalysts of various compositions (VBS-33, VBS-44, VBS-55, VBS-66) were developed (Ziyadullaeva, K.Kh., Nurmanov, S.E., Kurbanova, A.Dz., Akhmedova, N., 2021).

In Uzbekistan, ethane, propane-butane fractions, and gas condensates are prioritized as raw materials for the thermal pyrolysis of hydrocarbons. The study examined heavy fractions of liquid and solid pyrolysis products, secondary gas chemical products, and the chemical composition of pyrolysis distillate. The analysis showed that the secondary products isolated from heavy pyrolysis are liquids with a strong odor, appearing as dark brown, grease-like fluids, while the composition of the obtained pyrolysis feedstock is unstable.

To utilize liquid pyrolysis products as secondary raw materials and develop technology for their processing, work was conducted to study the chemical composition of pyrocondensate produced at the Ustyurt Gas Chemical Complex.

Table 1. *Chemical Composition of Pyrolysis Distillate*

Number of Carbon Atoms	Alkanes	Dienes	Olefins	Cycloalkanes	Arenes	Total
5	0.8	0.89	4.91	0.19	0	6.79
6	0.22	0.41	3.87	0.41	32.94	37.85
7	0.25	0.14	0.84	0.45	11.23	12.91
8	0.12	0.08	0.18	0.48	9.75	10.61
9	0.04	0.1	0.04	0.15	7.56	7.89
10	0.03	0.11	9.07	0.4	5.23	14.84
11	0.18	0.69	2.95	0	0.47	4.29
12	0	0.15	1.84	0	0	1.99
Total	1.64	2.57	23.7	2.08	67.18	97.17

The fractions of naphthalene and its homologues were isolated from heavy pyrolysis resins using dealkylation and rectification methods. The production of naphthalene is based on local raw materials, which positively impacts the overall efficiency of the heavy pyrolysis resin processing. However, the main challenge in effectively utilizing heavy pyrolysis products is related to the presence of asphaltenes and mechanical impurities in their composition.

The isolated products from heavy pyrolysis oils are odorless and depend on the composition of the original raw materials. Pyrocondensates from heavy pyrolysis products, containing indene and naphthalene, enable the synthesis of phthalic anhydride based on them (Kodirov, O.Sh., Ziyadullaeva, K.Kh., 2020).

Table 2. *Qualitative and Quantitative Composition of Heavy Pyrolysis Resin Samples*

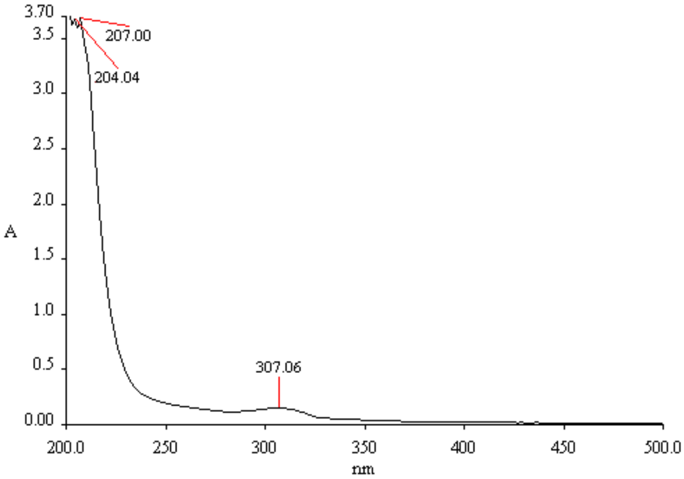
No.	Substance	Amount (%)	Degree of Correspondence	Retention Time (minutes)
1	Indene	9.33	93	12.30
2	1-Methylindene	8.96	96	14.72
3	Naphthalene	41.51	90	15.47
4	1-Methylnaphthalene	8.61	97	17.59
5	2-Methylnaphthalene	16.25	96	17.34
6	1-Ethylnaphthalene	1.77	90	18.78
7	1,6-Dimethylnaphthalene	1.71	95	19.18

The qualitative and quantitative composition of heavy pyrolysis resin samples was studied. The research was conducted using an Agilent 5977-A gas chromatograph equipped with a 30 m × 0.25 mm column, and the composition of the prepared sample was analyzed using gas chromatography-mass spectrometry (GC–MS). The results are presented in Table 2.

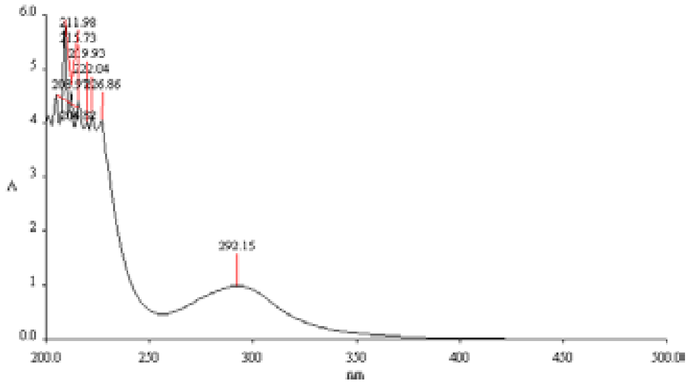
In the construction industry, superplasticizers are used to control the process and formation of structures, as well as the rheological properties of organic chemical additives — concentrated suspensions. This allows for targeted modifications of the flow properties of raw material mixtures and the properties of finished products.

Based on this, a superplasticizer was synthesized from naphthalene derived from secondary raw materials. The resulting hydrolyzed polyacrylonitrile, the synthesized superplasticizer, and the diluted superplasticizer were analyzed using UV spectroscopy (see Figure 1).

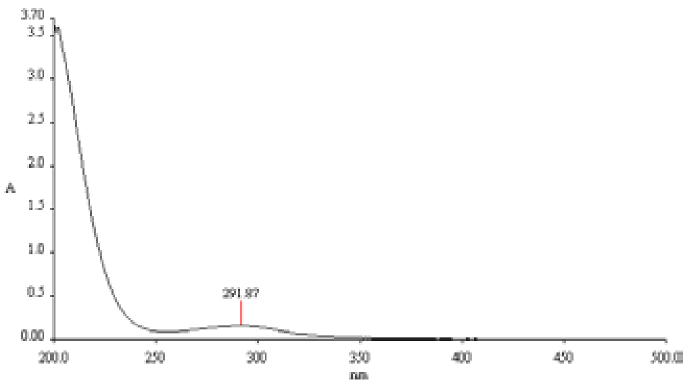
Figure 1.



A) Hydrolyzed Polyacrylonitrile



B) Synthesized Superplasticizer



C) Melted Superplasticizer

For the testing of superplasticizers, dry construction materials were selected: Portland cement grade PS400 D-20, gypsum, and cement with a high aluminum content. The influence of superplasticizers on the properties of these products was studied (see Table 3).

Table 3. *Test results for cement with synthesized superplasticizer*

No.	Mass of cement, g	Amount of additives by mass of cement, %	W/C (water-to-cement ratio)	Average density, g/cm³	Density after 28 days, MPa
1	100	–	0.31	2.065	25
2	100	0.05	0.30	2.05	25
3	100	0.2	0.29	2.142	27
4	100	0.5	0.28	2.12	28
5	100	0.8	0.27	2.15	30
6	100	1	0.27	2.192	31

Superplasticizers were added in an amount of up to 1% by weight of the binder. Adding superplasticizers in amounts greater than 1% generally led to a decrease in cement strength.

Table 4. *Results of Testing Cement Pastes with Synthesized Superplasticizer and High Aluminum Content*

No.	Mass of cement, g	Amount of additives by mass of cement, %	W/C (water-to-cement ratio)	Average density, g/cm³	Density after 28 days, MPa QMQ310–2003
1	100	–	0.43	6	37
2	100	0.02	0.43	6	38
3	100	0.2	0.43	7	42
4	100	0.5	0.43	8	45
5	100	0.8	0.43	11	50
6	100	1	0.43	13	54
7	100	1	0.39	6	66

The analysis of the obtained results shows that the addition of superplasticizer to the mix, while maintaining a constant water-to-cement ratio, increases the strength of the product, and the average density of cement particles rises with the increased amount of superplasticizer. This indicates the strength of the cement mixture and improvements in its performance characteristics.

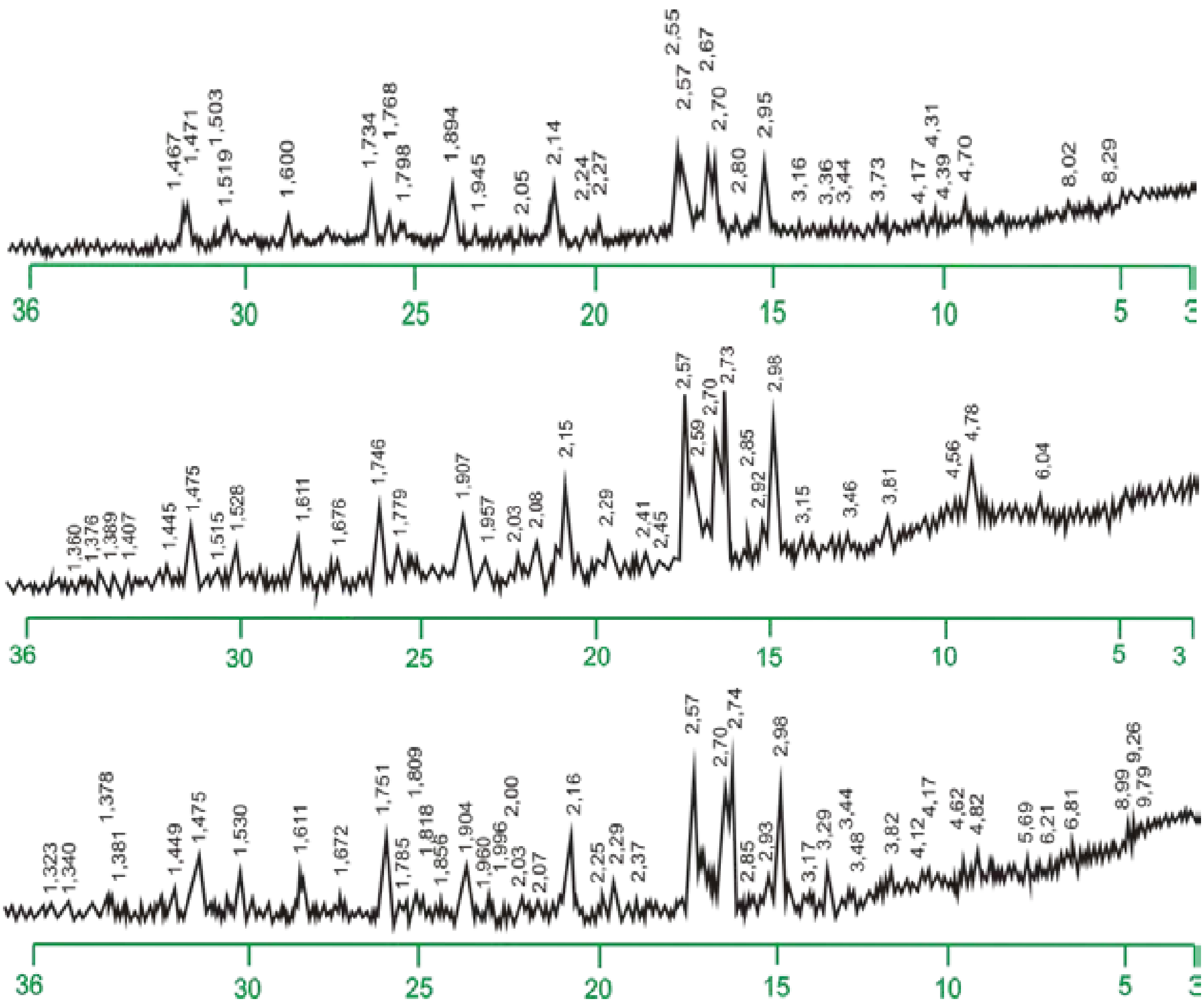
As seen in Table 4, the flowability of the cement with high aluminum content is 13 cm when a superplasticizer is added. Comparing these results with those of ordinary cement compositions showed an increase in plasticity. According to the literature, this is related to the high content of tricalcium aluminate. A study on the production of superplasticizers based on pyrocondensate-pyrolysis products was conducted, and cement mixtures with superplasticizers were investigated. Their results are presented in Table 5.

The analysis of the results revealed that a distinctive feature of the superplasticizer is that its use leads to normal setting of the cement mixture, resulting in the formation of a fine crystalline structure. Additionally, according to X-ray analysis of the binder samples, superplasticizers do not affect the composition of the hydrated phases on the surface of the cement.

Table 5. *Results of Testing Synthesized Superplasticizer and Gypsum Pastes*

No.	Mass of cement, g	Amount of additives by mass of cement, %	W/C (water-to-cement ratio)	Average density, g/cm³	Density after 28 days, MPa
1	100	–	0.5	8	11.6
2	100	0.03	0.5	8	16.1
3	100	0.2	0.5	9	15
4	100	0.5	0.5	10	13.3
5	100	0.8	0.5	11	12
6	100	1	0.5	13	11

Figure 1. *X-ray Spectrometer for Superplasticizers*



At the same time, the superplasticizer also exerts a moderate plasticizing effect. As the amount of superplasticizer increases, the density rises from 11.6 MPa to 16.1 MPa. Conversely, when the amount of additives relative to the mass of gypsum increases from 0.2% to 1%, the density of the mixture decreases from 15 MPa to 11 MPa.

Conclusions

The main content of the pyrolysis distillate consists of 67.18% arenes with carbon atom counts ranging from 6 to 12, and 23.7% olefins, allowing for the extraction of naphthalene and indene from the distillate. Naphthalene, indene, and their homologues were isolated from the heavy pyrolysis oils of gas processing plants, leading to the development of plasticizers for concrete and cement.

Additionally, the influence of various catalyst compositions on superplasticizers during the extraction of indene and naphthalene from heavy pyrolysis products was investigated and analyzed. The chemical composition of the heavy pyrolysis distillate, as well as the qualitative and quantitative composition of the samples of heavy pyrolysis oils and the test results of cement with synthesized superplasticizer, were studied. The structure of the obtained substances and their physicochemical properties were confirmed using various methods.

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Contact: kamola ziyadullayev@mail.ru, safarov1968@rambler.ru, anvar_ziyadullayev@mail.ru, eshpulatovmuhammad018@gmail.com