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OBTAINING SUPERPLASTICIZERS BASED ON PYROLYSIS COARSE TAR PRODUCTS

Annotation

The process of obtaining naphthalene, indene and phthalic anhydride based on 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 of processing of their fraction has been determined. Superplasticizers-additives for cement have also been created, their strength, the average density of cement particles, the influence of the amount of superplasticizers and the duration of their operation on the properties of the material have been studied.

Key words: Pyrolysis heavy distillate, naphthalene, indene, phthalic anhydride, superplasticizer.

ПОЛУЧЕНИЕ СУПЕРПЛАСТИФИКАТОРОВ НА ОСНОВЕ ПРОДУКТОВ ПИРОЛИЗА

Аннотация

Реализован процесс получения нафталина, индена и фталевого ангидрида на основе перегонки жидкой и твердой фракций тяжелых продуктов пиролиза, определен количественный и качественный состав образцов смол и продуктов переработки их фракции. Также созданы суперпластификаторы-добавки к цементу, изучены их прочность, средняя плотность частиц цемента, влияние количества суперпластификаторов и продолжительности их действия на свойства материала.

Ключевые слова*:* Тяжелый пиролизный дистиллят, нафталин, инден, фталевый ангидрид, супер пластификатор.

OG‘IR PIROLIZ MOYLARI ASOSIDA SUPERPLASSIFIKATORLAR OLISH

Annotatsiya

Og‘ir piroliz mahsulotlarining suyuq va qattiq fraksiyalarini distillash asosida naftalin, inden va ftal angidrid olish jarayoni amalga oshirildi, smola namunalari hamda ularning fraksiyasini qayta ishlash mahsulotlarining miqdoriy va sifat tarkibi aniqlandi. Sement uchun superplassifikatorlar va katalizatorlar yaratilgan, ularning mustahkamligi, sement zarrachalarining o‘rtacha zichligi, moddalar miqdori va ularning ishlash muddatining material xossalariga ta’siri o‘rganilgan.

Kalit so‘zlar: Og‘ir piroliz distillati, naftalin, inden, ftal angidrid, superplassifikator.

Introduction. The purpose of pyrolysis processes, which are extremely common in modern world petrochemistry, is to obtain lower olefins, mainly ethylene, they are a valuable raw material for the synthesis of the most important petrochemical products [1].

During pyrolysis, ethylene, propylene, butylene and butadiene, a significant amount of benzene, aromatic hydrocarbon derivatives such as toluene, xylene, indene, naphthalene, anthracene are released. Ethylene obtained by pyrolysis is used for the production of ethylene oxide, ethyl alcohol, polymers, styrene, plastics and other products. The main areas of use of liquid pyrolysis products are the production of benzene and other aromatic hydrocarbons, oils from polymer resins, diesel fuels, carbon, and high quality coke [4].

To improve the quality of the cement composition, it is important to use highly effective plasticizing additives. In the construction industry, to regulate the processes of structure formation and rheological properties of concentrated suspensions, superplasticizers are used - chemical additives that allow you to change the mobility of raw materials and the properties of finished products. One of the urgent tasks today is the search for new effective additives that allow you to change the interface and change the rheological properties of the dispersion [8].

Research methods. For the first time, catalysts of the VBS-33, VBS-44, VBS-55, VBS-66 types have been created for the separation of naphthalene and indene fractions from secondary products of gas chemistry at various temperatures and the production of plasticizers. UV spectroscopy, Raman spectroscopy, gas chromatography, mass spectrometry, differential thermal analysis-DTA methods were used in the work. Heavy pyrolysis oil from gas processing plants, naphthalene, indene and their homologues, plasticizers for concrete and cement, phthalic anhydride, naphthalene.

Analysis of the results. The main direction of the economic development of the Republic is the development of natural resources, their use, large-scale modernization of industrial production, technical and technological renewal, the introduction of modern scientific achievements and progressive innovative technologies in production, the creation of competitive, import-substituting products with stable demand in the world market.

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 total annual production capacity of the complex is 387 thousand tons of polyethylene and 83 thousand tons of polypropylene. This produces more than 102 thousand tons of pyrolysis distillates, 8 thousand tons of pyrolysis oil and 10 thousand tons of resin. pyrolysis distillates, pyrolysis oils and resin products generated in this process are not recycled.Pyrolysis distillates and pyrolysis oils naphthalene, aromatic hydrocarbons are currently the main secondary raw materials for the production of valuable chemical products needed for industrial needs. The processing of heavy fractions of liquid pyrolysis products and the introduction of these products into practice in the future are considered relevant, allowing the production of expensive and necessary products based on modern technologies. Due to the lack of acceptable technologies for the processing of pyrolysis waste for the production of indene, naphthalene and its homologues, phthalic anhydride is not produced in the country. Therefore, research aimed at developing technologies for processing waste from gas chemical complexes is an urgent task and requires its own solution.

Pyrolysis distillate and pyrolysis oil, as well as heavy fractions of liquid pyrolysis products, are secondary raw materials with great potential for the production of naphthalene, aromatic hydrocarbons, indene, phthalic anhydride and other valuable chemical products.

At present, modern technology allows us to produce expensive and necessary products. Due to the lack of acceptable technologies for the processing of pyrolysis waste for the production of indene, naphthalene and its homologues, phthalic anhydride is not produced in our country. Therefore, research aimed at developing an integrated technology for processing waste from gas chemical complexes operating in the republic is an urgent task and requires its solution.

The process of thermal pyrolysis of hydrocarbon raw materials is the main method for obtaining low molecular weight unsaturated hydrocarbons - olefins (alkenes) - ethylene and propylene. The main areas of use of liquid pyrolysis products are the production of benzene and other aromatic hydrocarbons, naphthalene, petroleum polymers, gasoline, raw materials for the production of high quality coke, etc.

Currently, due to the reduction in oil production in the petrochemical industry, the problem of expanding the raw material base for the production of aromatic hydrocarbons and their various derivatives is exacerbated. Heavy pyrolysis products indene and naphthalene, as well as their homologues, are of great interest as a potential raw material for the production of petrochemical products.

Secondary gas chemical products at different temperatures were separated into naphthalene and indene fractions. Based on the obtained products, catalysts of various compositions (VBC-33, VBC-44, VBC-55, VBC-66) were created [6].

In Uzbekistan, ethane, propane-butane fractions and gas condensates are the priority raw materials for thermal pyrolysis of hydrocarbons. In the course of the study, heavy fractions of liquid and solid pyrolysis products, secondary gas chemical products, and the chemical composition of the pyrolysis distillate were studied. Analysis of the results showed that the secondary products isolated from heavy pyrolysis are a liquid with a pungent odor, in the form of a dark brown fat-like liquid, and the composition of the resulting pyrolysis raw material is unstable.

In order to use liquid pyrolysis products as secondary raw materials and develop a technology for its processing, work was carried out to study the chemical composition of pyrocondensate produced in the Ustyurt Gas Chemical Complex.

Table 1.

Chemical composition of pyrolysis distillate

Number of carbon atom	Alkanes	Dienes	Olefins	Cycloalkanes	Arenas	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

Fractions of naphthalene and its homologues were isolated from heavy pyrolysis resin by dealkylation and rectification. The production of naphthalene is carried out on the basis of local raw materials, which positively affects the efficiency of the entire process of processing heavy pyrolysis resin. At the same time, the main problem of the effective use of heavy pyrolysis products is associated with asphaltenes and mechanical impurities in its composition.

The isolated products from heavy pyrolysis oils are odorless and depend on the composition of the feedstock. Pyrocondensates from heavy pyrolysis products containing indene and naphthalene make it possible to synthesize phthalic anhydride on their basis [7].

Table 2

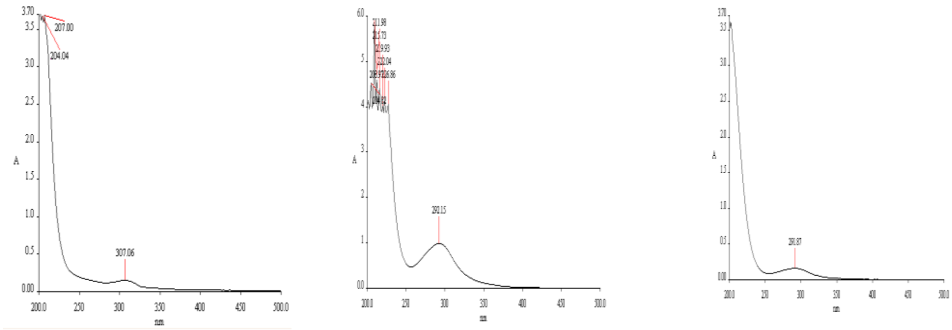
Qualitative and quantitative composition of heavy pyrolysis resin samples

	Substances	Quantity, %	Compliance degree	Retention time, minutes
1	Inden	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-ethyl naphthalene	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 studies were carried out using an Agilent 5977-A 30m × 0.25mm gas chromatograph, the composition of the prepared sample was analyzed by chromato-mass spectroscopy, the results are shown in **Table 2.**

In the construction industry, superplasticizers are used to control the process and structure formation and rheological properties of organic chemical additives-concentrated suspensions, which make it possible to purposefully change the fluidity of mixtures of raw materials and the properties of finished products.

Based on this, in the course of the work, a superplasticizer was synthesized based on naphthalene, obtained from secondary raw materials of production. The resulting hydrolyzed polyacrylonitrile, the synthesized superplasticizer, and the diluted superplasticizer were analyzed by UV spectroscopy (Fig. 1).



A) Б) C)

a) hydrolyzed polyacrylonitrile; b) synthesized super plasticizer; c) molten super plasticizer.

Portland cement grade PS 400 D-20, gypsum and cement with a high aluminum content were chosen as a dry building material for testing superplasticizers, and the effect of superplasticizers on the properties of these products was studied **(table 3)**.

Table 3

Test results of cement with synthesized superplasticizer

№	Mass of cement, g	The number of additives by weight of cement, %	W/C ratio	Average density, g/cm^3	Density after 28 days, MPa
	100	-	0.31	2.065	25
	100	0.05	0.30	2.05	25
	100	0.2	0.29	2.142	27
	100	0.5	0.28	2.12	28
	100	0.8	0.27	2.15	30
	100	1	0.27	2.192	31

Superplasticizers were added up to 1% by weight of the binder. The addition of superplasticizers by more than 1% in most cases led to a decrease in the strength of the cement.

Table 4

Test results of cement pastes with synthesized superplasticizer and high aluminum content

№	Amount of cement, g	The amount of additives by weight of cement, %	W/C ratio	Average density, g/cm^3	Density after 28 days, Mpa ***QMQ 310-2003***
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 by adding a superplasticizer to the mass at a constant water-cement ratio, the strength of the product increases, and the average density of cement particles increases with an increase in the amount of superplasticizer, which indicates the durability of the cement mixture, and the duration of its operation improves.

As can be seen from Table 4, with the addition of a superplasticizer, the fluidity of high-aluminum cement is 13 sm. Comparison of these results with conventional cement compositions showed an increase in plasticity. Based on the literature data, we can say that this is due to the high content of tricalcium aluminum. The production of superplasticizers based on pyrocondensate-pyrolysis products was studied, cement mixtures with superplasticizers were studied, their amount in gypsum mixtures after testing **table 5**.

Table 5

Test results of the synthesized superplasticizer and gypsum pastes

№	The amount of gypsum, g	The number of additives in relation to the mass of gypsum,%	W/C ratio (water cement ratio)	Distribution sm	Density after 28 days, MPa
	100	-	0.5	8	11.6
	100	0.03	0.5	8	16.1
	100	0.2	0.5	9	15
	100	0.5	0.5	10	13.3
	100	0.8	0.5	11	12
	100	1	0.5	13	11

Analysis of the results showed that a feature of the superplasticizer is that with its participation, the normal hardening of the cement mixture occurs with the formation of a fine crystalline structure. Also, according to X-ray analysis of samples of the binder plasticizer, superplasticizers do not affect the composition of the hydrated phases on the cement surface.

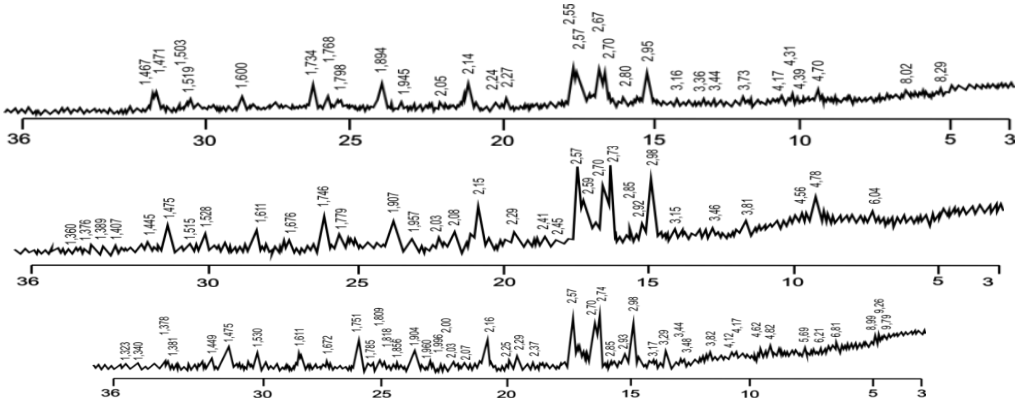


Figure 1. RFA Spectrometer of Superplasticizers

At the same time, the superplasticizer also has an average plasticizing effect, with an increase in the amount of superplasticizer, the density increases from 11.6 MPa to 16.1 MPa, with an increase in the amount of additives compared to the mass of gypsum from 0.2 to 1%, the density of the mixture decreases from 15 up to 11 MPa.

Conclusions. The pyrolysis distillate mainly contains 67.18% arenes with the number of carbon atoms 6-12 and 23.7% olefins, which makes it possible to isolate naphthalene and indene from the distillate. Naphthalene, indene and their homologues were isolated from the composition of heavy pyrolysis oils of gas processing plants, and plasticizers for concrete and cement were also obtained.

At the same time, the influence of catalysts of different compositions on superpassivators in the process of extracting indene and naphthalene substances from the composition of heavy pyrolysis products, the chemical composition of heavy pyrolysis distillate, the qualitative and quantitative composition of samples of heavy pyrolysis oil and the test results of cement with synthesized superplasticizer were studied and analyzed. The structure of the resulting substances and their physico-chemical properties have been proven using various methods.

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