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Synthesis of superplasticizer for concrete mixtures based on naphthalene

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Abstract. In subsequent years the construction industry in our country is developing very rapidly. Accordingly, the requirements for the rational and efficient use of raw materials and energy resources in building materials are also increased. To effectively solve the problem of developing prefabricated, monolithic concrete and reinforced concrete structures with high strength and durability of concrete mixtures, and special chemical additives, the widespread use of superplasticizers is required. In particular, obtaining such products based on industrial secondary raw materials is more important.
Pyrolysis of hydrocarbon raw materials is the main method for obtaining low molecular mass olefins, mainly ethylene, propylene, and acetylene. The increasing production of ethylene and propylene has also led to increasing by-products generated in this process. A large amount of pyrolysis oil as a by-product is also obtained at pyrolysis.
During the investigation, a naphthalene fraction was isolated from this product, and on its basis, a synthesis of superplasticizer for concrete mixtures was carried out.

1 Introduction

The development of the construction industry in recent years has led to increasing demand for chemical products. Many of the additives used in the production of building materials are chemicals. To create a solid foundation for the long-term sustainable development of all areas of the chemical industry, it is necessary to accelerate the process of transformation of the industry based on the best world practices. Creating multi-level value chains from raw materials to finished products based on new facilities for producing semi-finished products from local raw materials, including through organic synthesis and nanotechnology, will improve product quality and reduce their cost. At the same time, it is necessary to gradually reduce the export of unprocessed secondary raw materials through the organization of deep processing in the country [1].

The Ustyurt gas chemical complex of Uz-KorGaz Chemical LLC, the largest manufacturer of polymer products in Central Asia, pyrolysis of ethane and propane-butane fractions is carried out separately and, accordingly, ethylene, propylene, and then granulated polyethylene and polypropylene obtained by polymerization are used as commercial raw materials. The process will produce 102,000 tons of pyrolysis distillate,

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8,000 tons of pyrolysis oil, and more than 10,000 tons of residual solids as by-products [2]. As a result of the processing of this raw material, it is possible to obtain many products needed for various industries.

Due to the high content of naphthalene in pyrolysis oil, one of the important areas of its use is the production of plasticizers for concrete mixtures. Superplasticizers-polymer additives are widely used to increase the plasticity of concrete materials without reducing their strength. In terms of chemical plasticizers, the products are formaldehyde condensate of naphthalene sulfonic acid, melamine-formaldehyde condensate, and products of modification lignosulfonates [3, 4].

Another feature of these copper plasticizers is an increase in the material's flexibility, a reduction in cement consumption by 20%, water consumption by 30%, and an increase in its resistance to external influences. Reduces energy consumption by 2-3 times by increasing the product's flexibility. Currently, more than 1.25 million tons of superplasticizers are produced annually worldwide. This figure is increasing year by year. Several S-3, SMF, Dophen DF, Kratasol, Superplast, Polyplast, Ferrocrit, Vilacom, Reobuild 2000 (Russia); Agiplast (Rhone, France); Cormix (Rhodia, UK); The main components of superplasticizers such as Chriso Fluid (Chriso Industries, USA) are produced based on polymethylene naphthalene sulfonic acid.

The study considers the synthesis of superplasticizers based on local raw materials - secondary raw materials for the hydrolysis of pyrolysis hydrocarbons.

2 Methods

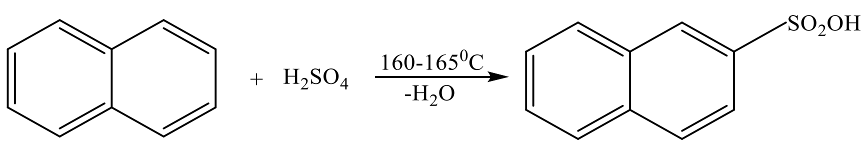
The main raw material was the naphthalene fraction obtained in the range of 210-230°C from pyrolysis oil, a secondary product of the Ustyurt gas chemical complex of Uz-KorGaz Chemical LLC. A laboratory plant for the sulfonation of the naphthalene fraction and a sealed plant for polycondensation were used.

To study obtained results, methods of physical-chemical analysis were used, and the composition of the superplasticizer was determined from the IR spectrum.

3 Results and discussion

The process of obtaining superplasticizers consists of the following steps:
- sulfation of naphthalene fraction;
- polycondensation of the obtained sulfomass with formalin;
- neutralization of polycondensation products.

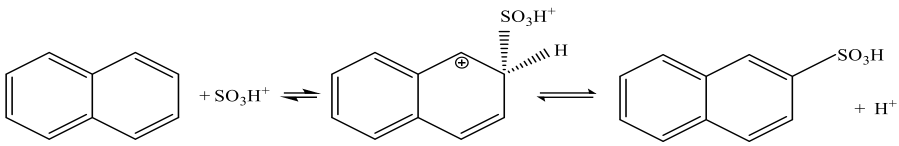
Sulfation of the naphthalene fraction 64 g of naphthalene fraction (fraction 210-230°C) was placed in a three-necked flask equipped with a mechanical stirrer, dropping funnel, and reflux condenser, heated to 140°C and liquefied, and a 98% solution of 60 g sulfuric acid was instilled will rate of 3 ml /min Since the process was exothermic, the temperature rose to 160-165^{0}C. In this case, the process lasted 4 hours. The reaction equation looks like this:



Process mechanism:

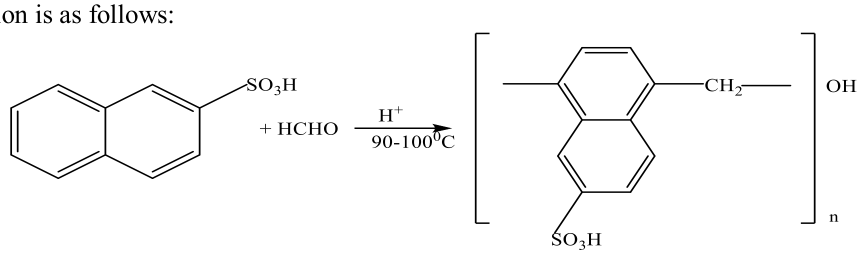
$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$

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



As a result of the reaction, sulfuric naphthalene acid was synthesized with a yield of 92%. Excess naphthalene is displaced by water vapor.

β- polycondensation of naphthalenesulfonic acid with formalin (35%). The process was carried out in a sealed reactor equipped with a mechanical stirrer. To carry out the reaction, b-naphthalenesulfonic acid and formaldehyde were used in a ratio of 1:0.8 mol, and the process was carried out at 90-100 0C for 6 hours. As a result, polymethylene naphthalene sulfonic acid was synthesized with a yield of 82.4%. The scheme of the polycondensation reaction is as follows:



Process mechanism:

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

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

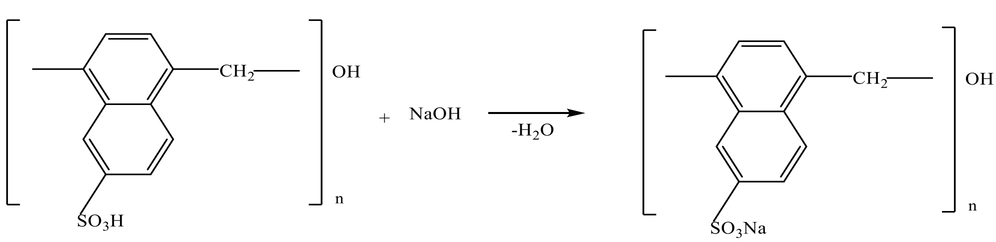
$$H_3SO_4^+ \rightleftharpoons H_2SO_4 + H^+ \qquad \text{III.}$$

$$CH_2O + H^+ \longrightarrow {}^+CH_2OH \qquad \text{IV.}$$

$$ArH + {}^+CH_2OH \longrightarrow \begin{cases} Ar\text{-}CH_2^+ + H_2O \\ Ar\text{-}CH_2\text{-}OH + H^+ \end{cases} \qquad \text{V.}$$

$$Ar\text{-}CH_2^+ + Ar\text{-}H \longrightarrow Ar\text{-}CH_2\text{-}Ar + H^+ \qquad \text{VI.}$$

Neutralization of polycondensate. The resulting oligomer was neutralized with 40% aqueous solution of sodium hydroxide. As a result, a 35% aqueous solution of sodium polymethylene naphthalene sulfonate was obtained. The reaction equation is as follows:



The effect of the resulting polymer product on the strength of concrete and the plasticity of the concrete mix as a superplasticizer (SP) has been studied.

For this 4 compounds were used for obtain composition were obtained:

1 for a composite control

2 compound 0.4% SP,

3 compound 0.6% SP,

4 compound 0.8% sp.

In the experiment, it was achieved that the rate of decrease in the height of the concrete mixture was one case, i.e., 18 cm (Table 1).

Table 1. The composition of concrete mixtures

№	Cement (g)	Sand (g)	Gravel (g)	Water (g)	SP cement (%)	Decrease in height of concrete mixture, sm
1	2660	8750	3990	1115	-	18
2	2660	8750	3990	935	0,4	18
3	2660	8750	3990	845	0,6	18
4	2660	8750	3990	725	0,8	18

The change in water consumption is registered in the following graph.

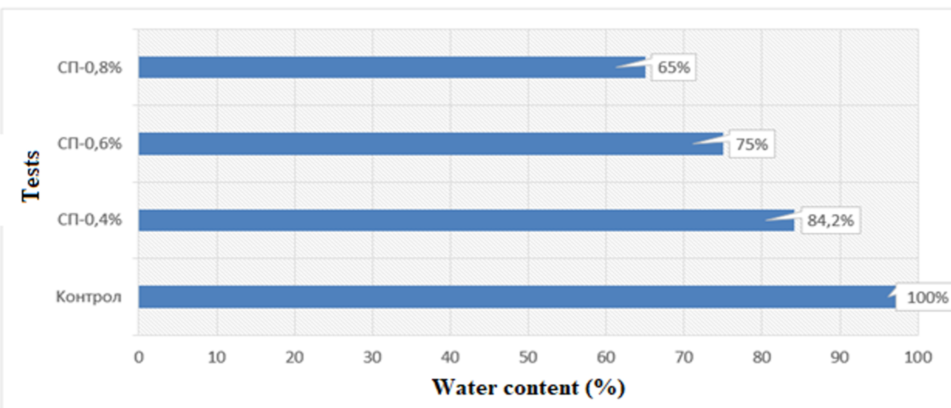


Fig. 1. Amount of water used for concrete mixture, %

Revealed was a decrease in the mass of water consumed when using the joint venture concerning the mass of water obtained for control. For example, the water content decreased by 16.2% with the addition of 0.4% SP, by 25% with the addition of 0.6%, and by 35% with the addition of 0.8% (Fig.1).

The obtained concrete samples were poured into molds 10x10x10 cm in size, and after 7 days, their strength was determined according to the GOST 10180-2012 GOST-TEST on factory machine No. 082020224 (Table 2). Obtained results are presented in Figures 2-5.

Table 2. Strength of concrete mix samples according to GOST 10180-2012

For instance	Sample surface (S), mm^2	P_{max}, kN	Compressive strength limit, (R_{com}), MPa	Modulus of elasticity in compression (Ec), MPa
1 (Control)	10000	166.839	16.684	205.493
2 (СП-0.4%)	10000	201.423	20.142	143.128
3 (СП-0.6%)	10000	253.037	25.304	161.203
4 (СП-0.8%)	10000	326.919	32.692	274.540

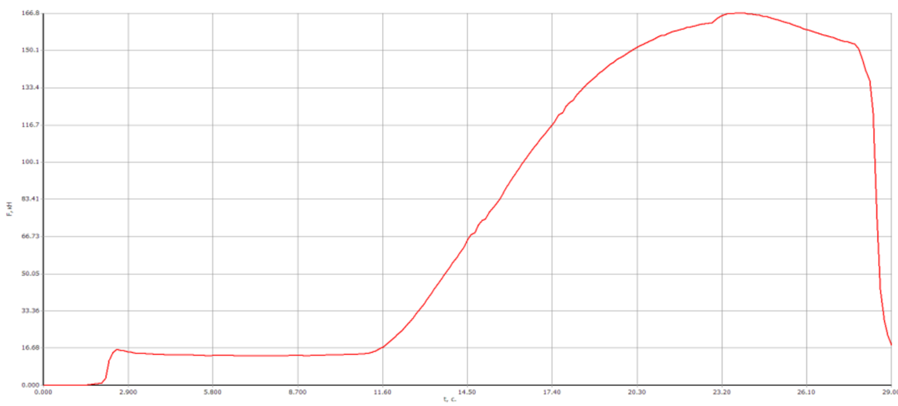


Fig. 2 Strength of a sample of 10x10x10 cm prepared for control

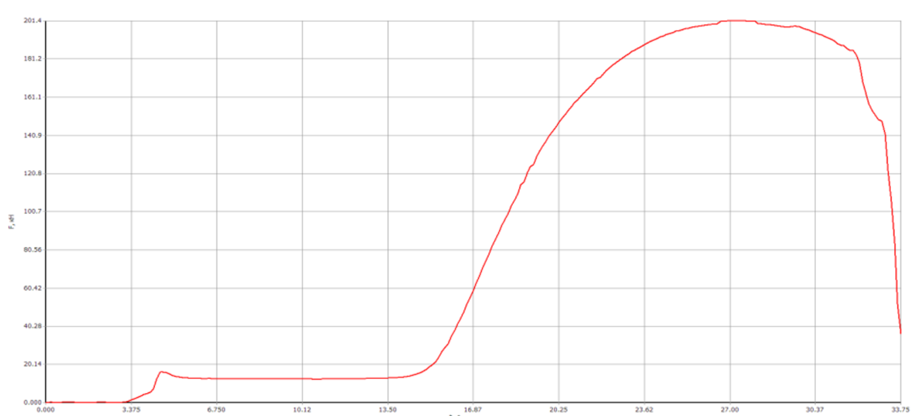


Fig. 3. Strength of a Sample of 10x10x10 Cm with the Addition of 0.4% Sp

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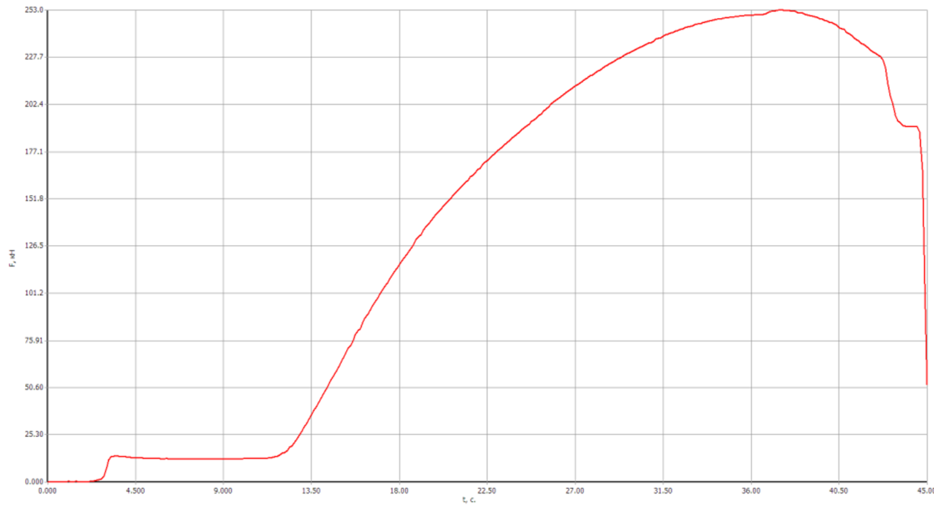

Fig. 4. Strength of a sample of 10x10x10 cm with the addition of 0.6% SP

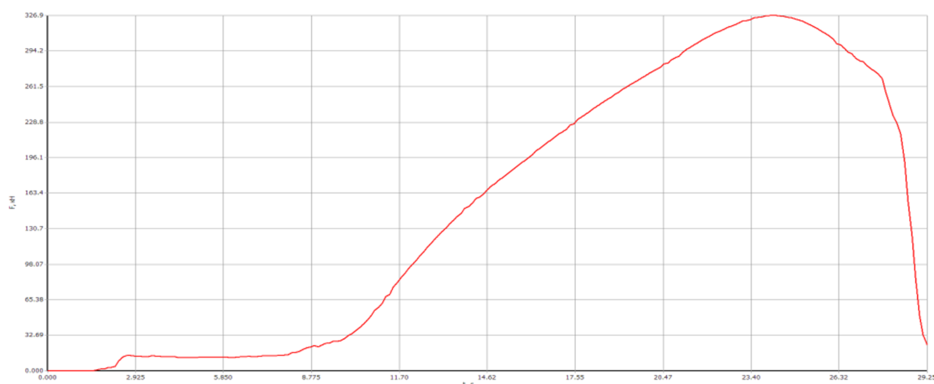

Fig. 5. Strength of a sample of 10x10x10 cm with the addition of 0.8% SP

The results obtained show that the strength of superplasticizer concrete mixtures obtained from the naphthalene fraction of pyrolysis oil in the range of 210-230 ° C increased by 17.2% after 7 days with the addition of 0.4%, 34.1% with the addition of 0.6% and 48 seconds with the addition of 0.8% an increase of 97% was found.

The IR spectrum of the resulting superplasticizer sodium polymethylene naphthalene sulfonate was obtained was analyzed (Fig. 6, Table 3).

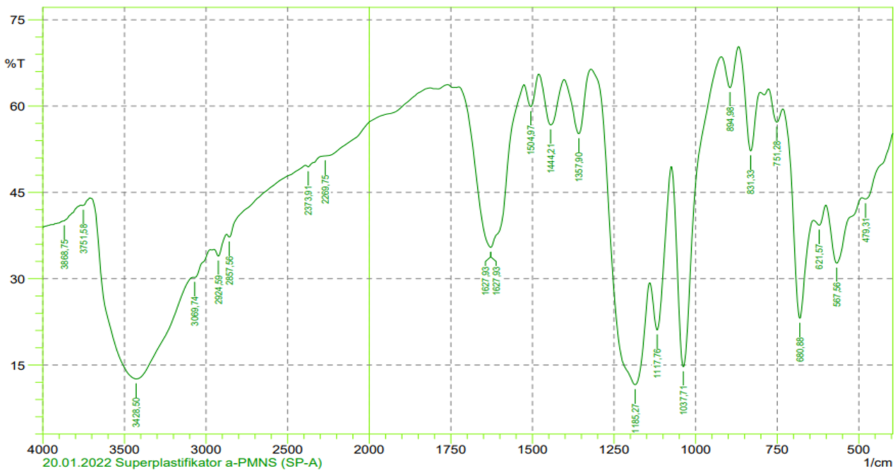

Fig. 6. IR spectrum of polymethylene naphthalene sulfonate sodium

Table 3. Absorption areas of the main groups of polymethylene naphthalene sulfonate sodium

Vibration frequency, cm^{-1}	Functional group	Type of vibrations
3428.5	-OH	valence
3069.74	aromatic core C-H	valence
2924.59	$-CH_2-$	asymmetric valence oscillation
2857.56	$-CH_2-$	symmetrical valence oscillation
1444.21	$-CH_2-$	deformational
1185.27	S=O	valence
1117.76	$-SO_3Na$	Valence
751.28	aromatic core CH	deformational
1504.97	interchangeable aromatic core	valence
1627.93	aromatic core	valence
1357.9	-OH	deformational

4 Conclusions

The composition of pyrolysis oil was studied, and a fraction based on naphthalene was isolated at 210–230 ^{0}C. β-sulfonaphthalene was synthesized by sulfonation of the resulting naphthalene. As a result of its polycondensation with formalin, sodium polymethyl naphthalene sulfonate was obtained.

By-product of the pyrolysis - a superplasticizer from pyrolysis oil was obtained, and it's positive effect on the flexibility and strength of concrete mixtures was determined.

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