

Improvement of Thermochemical Dewatering of Coal Tar by Forming Compositional Demulsifier

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Received April 5, 2021; Accepted September 7, 2021

Abstract

Aging of the coke oven batteries and a decreasing in coking periods lead to the growth in the density and water content of produced coal tar. The choice of proper chemical demulsifier for water decanting is of scientific and practical interest. Based on the analysis of the experience of separating crude oil emulsions, the feasibility of introducing a wetting and detergent additive was established. Especially it is of concern when the character of stabilization of the emulsion was changed and its rheological characteristics were deteriorated. The objective of the study was to develop a composition based on the nonionic demulsifier "PM-1441 oil-soluble" to increase its efficiency in the dehydration of coal tars with a high degree of pyrolysis. The separation efficiency of water-tar emulsions based on heavy coal tar was planned to be increased by giving polyfunctionality to the composition prepared on the basis of the successfully applied non-ionic demulsifier "PM-1441". The wetting effect of surfactants with respect to emulsion stabilizers was measured by the contact angle, and the washing effect was determined by the optical density of surfactant solutions after interaction with potential emulsion stabilizers. The universal additive surfactant "OS-25" was selected, which has both wetting and detergent properties. The composition has been developed on the basis of a nonionic demulsifier "PM-1441 oil-soluble" and ethoxylated alcohol "OS-25" in a mass ratio of 32/68 for dissolving the active substance in a 5% solvent based on ethyl alcohol. The specified composition allows more efficient dewatering of coal tar with a high degree of pyrolysis than when using the base reagent "PM 1441".

Keywords: Composite demulsifier; High pyrolysis coal tar; Emulsion stabilizers; Wetting and detergent properties.

1. Introduction

Spontaneous condensation of water vapor and tar during quenching and cooling of volatile coking products in the presence of soot particles, coal and semi-coke dust with mineral inclusions, as well as a change in the coking conditions for mixtures of different grades, causes the formation of coal tar of different quality. It can be assumed that the mechanism of stabilization of the "water-in-tar" emulsion is also changed, which in some cases leads to a decrease in the effectiveness of the nonionic demulsifier successfully used during the last years in Ukrainian coking plants.

On the other hand, the enlargement of the variety and the development of new demulsifiers serve as an illustration of the lack of a universal reagent for dehydration of constantly changing systems with various emulsion stabilizers. In industrial practice, on the contrary, it is more convenient to have a stock of the base demulsifier and promptly respond to a change in the nature of emulsions by introducing a small dose of various additives. In this case it is possible not only to use a previously purchased expensive reagent, but also to increase the degree of dehydration, reduce the consumption of the reagent in the case of synergism of the additives of the new demulsifier composition.

Therefore, it is of scientific and practical interest to develop general principles of composing such compositions in order to reduce the number of experiments set up by the "trial and error" method.

A review of literature data on the synergism of the constituent components of demulsifying compositions shows a different interpretation of the very concept of "synergism", in most cases it is understood as a simple improvement in the properties of the composition relative to the base substance. Strictly speaking, the synergism of the action of the components means that the property of the composition exceeds the value calculated by the additivity rule [1]. Nevertheless, even an additive increase in the effectiveness of the demulsifying composition is of practical value, especially if the second component is available on the market and reduces the cost of dehydration.

Mixing of surfactants is a widespread technique in various fields of their application: in the extraction of hydrocarbons from contaminated soils [2], wastewater treatment [3], separation of emulsions of lubricants and oils [4], the use of detergents [5], foaming agents, emulsifiers, cosmetics [6].

The complexity of the separation of "water-in-oil" emulsions is associated with a large number of natural stabilizers, an increase of heavy viscous oil production, and the use of new chemical reagents for the intensification of oil production, affecting the surface properties of systems. Therefore, at the present stage of field oil treatment, complex compositions of demulsifiers with high activity are used, which should have wetting, washing, peptizing and flocculating abilities [7].

More dense and viscous coal tar forms very stable emulsions, as they are stabilized by molecules with a higher degree of aromaticity and aggregation than petroleum ones. Dispersed substances insoluble in toluene, which are stabilizers of emulsions based on coal tar [8], have a greater number of carboxyl groups, have a higher degree of aromaticity, and contain more heavy components [9]. Therefore, for the separation of more stable emulsions based on coal tar, it is all the more relevant to develop compositions of demulsifier reagents that have a universal effect with respect to the variable nature of emulsion stabilizers.

Complex reagents are widely used for the thermochemical dewatering of coal tar emulsions. For example, a composition is including polyesters with a molecular weight of 3000-5000, nitrogen-containing polyesters, and silicone-containing polyesters, mixed in alcohol solvents [10]. It can be assumed that the demulsification effect is based on the joint action of one class of chemical compounds, which are modified with different functional groups to impart complex properties and varying degrees of hydrophobicity. This mixture is designed for dewatering of the semi-coking tar emulsion, which is characterized by a significantly lower degree of pyrolysis. The applicability of such compositions is also limited by the market of specific brands of reagents.

It is proposed to break coal tar emulsions by a composition containing a nonionic demulsifier with hydrophile lipophile balance (HLB) value ≥ 6.5 and anionic demulsifier ($HLB \geq 45$) in a mass ratio of 1: 1 [11]. In this composition non-ionic type of demulsifier is used as a base, and a highly soluble surfactant is used as an additive, which would most likely promote wetting and removing of mechanical impurities from the tar-water interface. The limitation of the application of this proposition is the mixing process of water and tar, which requires installation of tar extraction unit for mixing and subsequent settling of the coal tar emulsion. According to the available production experience of coal tar washing, the ratio of the water and tar phases must be $1:2 \div 3$, with a decrease in the amount of water, the risk of secondary watering of the treated tar increased.

Demulsifier compositions are often patented not only for separating oil emulsions, but also for mixtures of different nature. For example, demulsifiers, originally developed for the oil industry, are used in the by-product coke industry [12]. It can be assumed that, and the principles of the selection composite reagents for breaking oil emulsion can be extended to coal tar systems, taking into account certain specific features.

If the type of formed ions is taken as a classification criterion, then demulsifying compositions in most cases contain the main nonionic reagent - block copolymers of ethylene and propylene oxide, and as additives of ionic type surfactants - cationic or anionic [13-14]. A higher depth of dehydration was noted when using a mixture of nonionic surfactants with anionic (sodium alkyl sulfates) [15]. Studies of 37 demulsifiers according to this classification criterion [16]

have shown that anionic and nonionic demulsifiers are more effective than cationic ones. To increase the efficiency of cationic demulsifiers, calcium chloride is added to the composition [17].

According to the mechanism of demulsifier effect in dispersed systems, additionally introduced surfactants can be defined as wetting agents, dispersants, coagulants. Their use not only retains the properties inherent in individual components, but can also introduce new qualities into the composition [18]. The use of combinations of wetting agents, detergents, flocculants, depressants helps to remove finely dispersed particles from the tar-water surface of emulsions during the breaking emulsion of high viscous oils. Good activity was shown by the composition "demulsifier/detergent/wetting agent = 1/1/1", however, this ratio cannot be considered universal and the composition needs to be clarified in specific cases [19].

Demulsifying compositions can be formulated according to the principle of regulating hydrophilicity, for example, the activity of ethoxylated phenolic formaldehyde resins is regulated and modulated by mixing with a low molecular weight surfactant (ethoxylated nonylphenol) [20].

A similar principle of composing compositions based on relative solubility in water was applied when selecting a combination of oil and water-soluble reagents. It is interesting to note the demulsifier formula was based on a mixture of individual surfactants available on the market. Surfactants were dissolved in xylene or water, transparent solutions were chosen, and oil- and water-soluble reagents were combined to obtain a synergistic effect [21].

To regulate the polarity of polymeric demulsifiers based on polyalkylene-modified polydimethylsiloxanes, it is proposed to be guided by the molecular weight [22]. Compositions of demulsifiers can also be formulated according to the principle of linearity and branching of molecular chains [23].

To enhance the action of the main reagent, chemical substances of various classes are used: alcohols, aromatic compounds, carboxylic acids, aminocarboxylic acids, bisulfites, hydroxides, sulfates, phosphates, polyols and their mixtures [24]. The addition of alcohol promotes demulsification; it is believed that alcohol contributes to the destruction of the stabilizing film [25]. The addition of electrolytes improves the degree of demulsification [26]. Undoubtedly, developments on the involvement of local raw materials and intermediates as an improving component of a demulsifying composition are relevant, for example, saponification of cotton tar as a flocculant [27], the involvement of local resources of surfactants and sources for their production (vegetable oils, soaps, starch) [28]. Bacteria [29] and fungal spores [30] are tested as demulsifiers. This suggests that these additives are not universal and it is difficult to explain their effect, or at least predict their effect on the separation of coal emulsions.

Another important factor that changes the activity of a demulsifier in an aqueous medium is the acid-base balance, which can be expressed in terms of the pH value. It is believed that asphaltenes preventing the coalescence of water droplets in the emulsion have an amphoteric structure; they acquire a positive or negative charge depending on the pH of the medium. At high or low pH of the medium, they become more surface active and increase the stability of the emulsion. The best destruction of the emulsion occurs when the pH of the solution is close to a neutral reaction [31]. Disperse substances insoluble in toluene are believed to stabilize coal tar emulsions in the first one most of the nitrogen-containing, carboxyl and acid functional groups are concentrated [32].

On the other hand, the acid-base balance also affects certain classes of surfactants; the influence of alkaline agents on the effectiveness of polymer demulsifiers is known [33]. Therefore, it is necessary to take into account the influence of the pH of emulsion stabilizers and demulsifier at the same time.

The performed review, in our opinion, in relation to the watered coal tar, shows the suitability of changing the hydrophilicity of the reagent in the event of a change in the pyrolysis of the tar, or the introduction of a wetting and detergent additive when the nature of dust entrainment changes when the tar vapor leaves the coking chamber. The objective of the study was to develop a composition based on the nonionic demulsifier "PM-1441 oil-soluble" to increase its efficiency in the dehydration of coal tars with a high degree of pyrolysis.

2. Experimental

A high pyrolysis sample of the coal tar was selected to study the dewatering emulsion. The coal tar with a high-water content was sampled at an intermediate stage of dewatering and did not contain a demulsifier and external impurities. Coal tar quality indicators were determined by standardized methods of analysis in accordance with TU U 19.1-00190443-100: 2016 (Table. 1).

Table 1. Characteristics of coal emulsion

Specification		Value
Density at 20°C in terms of dehydrated coal tar, kg/m³		1261
Mass fraction of water, %		31.2
Mass fraction of substances in terms of dehydrated coal tar, %:	insoluble in toluene	20.3
	insoluble in quinoline	18.7
	ash	0.16

A nonionic reagent based on block copolymers of ethylene and propylene oxides "PM 1441" was used as the main demulsifier, the average molecular weight is 3000-3600, the average molecular weight of the polyoxypropylene block is 1750-2200 [12]. For comparison, reagents from Clariant Oil Services (Switzerland) were also used as a reference.

The choice of additive was carried out by selecting a surfactant from available commercial surfactants especially detergents and wetting agents. In general, wetting agents have an HLB index of 7-8, and detergents of 12-15, in addition, the type of reagents can be indicated on the manufacturer's websites. The characteristics of the investigated surfactants - additives are given in Table 2.

Table 2. Characteristics of surfactants as potential additives to demulsifying composition

Surfactant trade name	Surfactant class	Application area	Molecular weight	Number of oxyethylene groups
Tween 80	Polyethylene glycol esters of fatty acids and polyhydric alcohols	solubilizing agent	1 308	20
Sintanol DS-10	Oxyethylated fatty alcohols	detergent and wetting agent	609	9
Sintanol ALM-2	Oxyethylated fatty alcohols	detergent	273	2
PEG-200	Ethylene glycol polyoxyethylene glycol ethers	detergent	200	3
OS 25	Oxyethylated fatty alcohols	wetting agent, antistatic agent and detergent	1 369	25
Stearoks 6	Oxyethylated fatty acids	antistatic	464	6
Proxanol 268	Block copolymers of ethylene and propylene oxides	hydrophilic base in the production of cosmetics	14 068	260
OS 20	Oxyethylated fatty alcohols	antistatic	1 149	20
Proxanol TsL 3	Block copolymers of ethylene and propylene oxides	wetting agent	3 604	38
Ripox 6	Oxyethylated fatty acids	antifoam	462	6

A method for comparing the wetting ability of various surfactants with respect to organic substances involved in the stabilization of inverse emulsions is given in [7, 19]. The wetting ability of the solutions was evaluated in relation to the solid surface of naphthalene, as the main model component of coal tar, and to the assumed mechanical stabilizers of emulsions, i.e., to coal and coke. Surfactant solutions were prepared on a water basis with a concentration of 1 wt.%.

Evaluation of the wetting ability was carried out by measuring the contact angle by the "lying drop" method. A drop of a surfactant solution with a volume of 7 μdm^3 was placed on the investigated solid surface of emulsion stabilizers. Using a microscope, the dynamic diameters of the formed droplet circles were determined over time. The images were taken using a device with ToupTech, ToupView imaging software. The graphic determination of the contact

angle was carried out according to the obtained images by a circular method along the base line and tangent.

The washing activity of surfactants in relation to model surfactants was assessed by photometric evaluation of the optical density of solutions of various surfactants before and after the treatment of dispersed particles of the assumed solid stabilizers of emulsions. In contrast to the method [7], aqueous solutions of surfactants were used as a solvent, since the enterprise refused from a hydrocarbon aromatic solvent for dissolving a demulsifier due to premature wear of the pump seals, in the cavity of which the tar and demulsifier were mixed.

As emulsion stabilizers coal of grade "K" and commercial coke of grade "KDM1" were taken, crushed to a particle size of <0.05 mm, and naphthalene of grade "KhCh". An identical sample of solids weighing 3.00 g was placed in a flask with 25 ml of a surfactant solution. After vigorous shaking, the flask was kept at room temperature (29°C) for 24 hours. Next, the optical density of the filtered solution was measured on a spectrophotometer at a wavelength of 490 nm. The calculation of the relative washing ability (RWA) was carried out according to the formula: $RWA = \frac{D_2 - D_1}{D_3} \times 100\%$,

where D_1 is the optical density of an aqueous surfactant solution with a concentration of 1%; D_2 is the optical density of an aqueous surfactant solution after contact with a dispersed solid; D_3 is the maximum optical density of an aqueous surfactant solution in this series of experiments.

The relative washing activity of aqueous solutions of surfactants towards emulsion stabilizers was established relative to the maximum dissolution of one of the studied surfactants. For this, the optical density of surfactant solutions was determined in the presence and absence of solutes, the difference in values of which was used to judge the solubilization of model emulsion stabilizers.

The effectiveness of the developed composition for breaking emulsions was assessed using the bottle test method, which was introduced as internal standards in oil producing enterprises. During testing, the basic principles formulated in [34] were followed to: taking a representative sample, testing only a freshly taken sample, the same mixing conditions and the maximum complete identity of the tests.

3. Results and discussion

For the destruction of aggregates, which are blocked water drop coalescence, it is desirable that the complex of surfactants has a wetting and washing effect. The wetting effect of demulsifiers with respect to oil components is usually determined by the contact angle of wetting, and the washing effect is determined by determining the optical density of surfactant solutions after interaction with oil components. [7].

Table 3 shows the results of determining the contact angles of wetting, measured by the shape of drops of surfactant solutions on the surface of coal, coke and the crystalline surface of naphthalene on a glass slide formed during cooling of its melt. The solutions were prepared with a concentration of 1 g/dm³, equilibrium values were established, as a rule, within 1 min, the results were obtained by processing at least three images of drops taken in random order.

Table 3. Values of equilibrium wetting contact angles

Trade name of surfactant	Contact angle, degrees		
	coal	coke	naphthalene
Tween 80	38	54	55
Sintanol DS-10	30	34	41
Sintanol ALM-2	40	44	58
PEG-200	46	52	57
OS 25	41	53	54
Stearoks 6	35	45	56
Proxanol 268	52	53	56
OS 20	39	50	56
Proxanol TsL 3	47	56	57
Ripox 6	37	38	43

The results showed a high hydrophobicity of naphthalene as a model component, the content of which is highest of other individual components of the coal tar. The wettability of mechanical emulsifiers (coal and coke particles) is higher, both due to mineral inclusions and due to the content of heteroatoms (O; N; S). The smallest contact angles were shown by solutions of the following surfactants: "Sintanol DS-10", "Ripox 6", "Stearox 6", and "Sintanol ALM". No clear dependence of the value of the contact angle on the concentration of solutions was observed; as a rule, a concentration of 1 g/dm³ is sufficient to wet the investigated surfaces, a further increase in the concentration to 10 g/dm³ had practically no effect on the measured values of the contact angles. Table 4 shows the results of evaluation of the detergency of surfactant solutions towards the model substances under study.

Table 4. Relative washing activity of surfactants towards model emulsion stabilizers

Trade name of surfactant	Relative activity, %		
	coal	coke	naphthalene
Tween 80	76.6	14.9	3.5
Sintanol DS-10	48.0	13.0	2.6
Sintanol ALM-2	20.8	5.9	3.1
PEG-200	20.3	4.7	0.3
OS 25	98.5	15.5	2.2
Stearox 6	43.7	9.9	0.3
Proxanol 268	34.5	9.4	0.9
OS 20	73.5	18.9	1.8
Proxanol TsL 3	100.0	24.8	1.0
Ripox 6	0.3	1.0	3.4

Surfactants, which are characterized by lower HLB numbers and cloud points of solutions, have a higher affinity for hydrophobic naphthalene. The highest apparent solubility towards naphthalene has "Tween 80", "Sintanol ALM 2", "Ripox 6". The highest dissolution properties of coal substances were shown by "Proxanol TsL-3", "OS-25", "Tween 80", "OS-20".

Results have shown that it makes sense to prepare five compositions, including one wetting agent and one detergent from three potential wetting agents ("DS-10", "Ripox 6", "OS-25") and two potential detergents ("Proxanol TsL-3", "OS-25"). However, taking into account the current availability on the market, only one composition is rational, containing the universal substance "OS-25", which has both wetting and detergent properties.

To confirm the effectiveness of the selected composition, control mixtures were prepared (Table 5) with different contents of the main demulsifier PM 1441 and additives ("OS-25"). The experiments were carried out on a heavy coal tar sampled after the first stage of decantation; the water content of the emulsion was 15%. To compare the effectiveness, two demulsifiers from Clariant Oil Services (Switzerland) were used as markers, which previously showed a relatively good dewatering efficiency of coal tar emulsion. The dosage of demulsifiers in all experiments was 200 g/t of coal tar.

Table 5. Demulsifying compositions for tested emulsions

Parameter:	Composition number									
	1	2	3	4	5	6	7	8	9	10
Content of the composition	OS-25/PM 1441 mixture					Individual reagents				Blank test
OS-25 wt., %	17	29	57	73	89	100	-	-	-	-
PM1441 wt., %	83	71	43	27	11	-	-	-	100	-
Dissolvan	-	-	-	-	-	-	100	100	-	-

The test results of demulsifier compositions are shown in Fig. 1. As expected, the Dissolvan reagents (7,8), designed for the separation of heavy oils, showed high efficiency. In the experiment without a demulsifier, the release of water did not occur, which indicates the stability

of the tested emulsion. Basic nonionic demulsifier "PM 1441" showed insignificant efficiency. Compositions 3 and 4 showed encouraging results, which makes it possible to assume that the synergism of dehydration will be expected at approximate ratio "OS-25"/"PM 1441"=65÷80/ 35÷20.

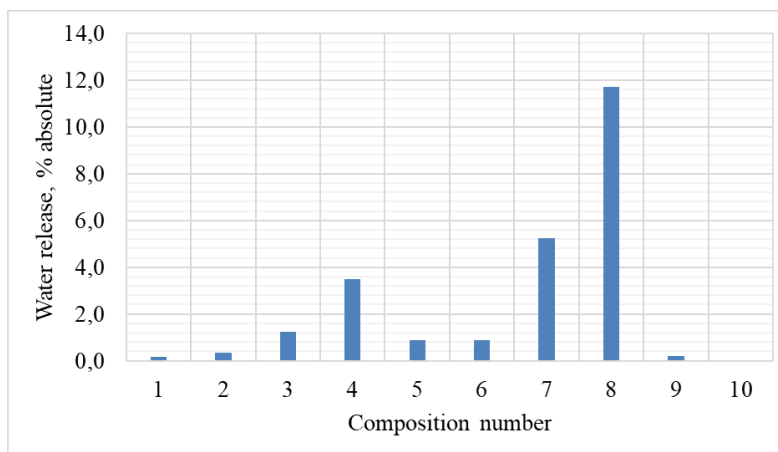


Fig. 1 Results of thermochemical dewatering of coal tar emulsion (numbering according to Table 5)

The effectiveness of demulsifying compositions is also influenced by their dosage; in some coke-chemical plants, the effectiveness of dewatering was recorded already at of 30 g/t. In some cases, the consumption of demulsifiers as much as 200 g/t may be insufficient. Therefore, it is necessary to study the effectiveness of the developed composition in the range of 50-250 g/t of reagent consumption.

The process of diffusion of the components of the demulsifier to dispersed water in the emulsion is influenced by the environment in which the active substance of the demulsifier dissolves. In preliminary experiments, demulsifiers were introduced in the form of an aqueous dispersion. Our earlier comparison of various demulsifiers during coal tar dewatering showed that dissolving of reagents in alcohols are more efficient. Therefore, it is of interest to study the effect of the solvent on the effectiveness of the designed compositions.

Based on the studies performed, the search for the optimal composition of the mixtures continued taking into account the influence of a narrower range of "OS-25"/"PM 1441" ratios, the consumption of demulsifier and the ratio of ethanol/water solvents. The concentration of the basic substance ("OS-25"+"PM 1441") in the solution was taken to be 5%. The selected factors satisfy the requirements of controllability, interdependence and one-valuedness, the planning area is given in Table 6.

Table 6. The area of factorial planning of the experiment

Factor	Factor code	Unit of measurement	Factor levels		
			-1	0	1
Concentration of "OS-25" in mixture	X ₁	%	30	60	90
Demulsifier dosage	X ₂	g/t	50	150	250
The concentration of ethanol in a mixture with water	X ₃	%	0	50	100

As the response function an absolute decrease in the moisture content of the water-in-tar emulsion, (W, %) was taken. To obtain the maximum amount of objective information about the effect of the selected factors on tar dewatering using the smallest number of observations, the Box-Behnken planning method was used. The design is a symmetric non-compositional three-level second-order design and is a combination of a two level (-1; +1) full factorial experiment with an incomplete block balanced design. In terms of a number of statistical characteristics, the Box-Behnken designs exceed the central compositional orthogonal and

rotatable designs, which are widely used in industrial experiments [35]. The planning matrix was generated by the STATGRAPHICS program and is presented in Table 7.

Table 7. Planning matrix and experimental data

Experiment number	X ₁	X ₂	X ₃	W, %
1	-1	-1	0	0,74
2	1	-1	0	3,76
3	-1	1	0	5,33
4	1	1	0	8,56
5	-1	0	-1	3,48
6	1	0	-1	6,71
7	-1	0	1	5,50
8	1	0	1	8,73
9	0	-1	-1	3,82
10	0	1	-1	9,03
11	0	-1	1	5,93
12	0	1	1	11,05
13	0	0	0	8,88
14	0	0	0	9,05
15	0	0	0	9,20

The significance of the model coefficients was checked using the Pareto diagram (Fig. 2), the horizontal columns that cross the vertical line of the 95% confidence level indicate the statistical significance of the following model coefficients: X₂, X₁₂, X₁, X₂₂, X₃.

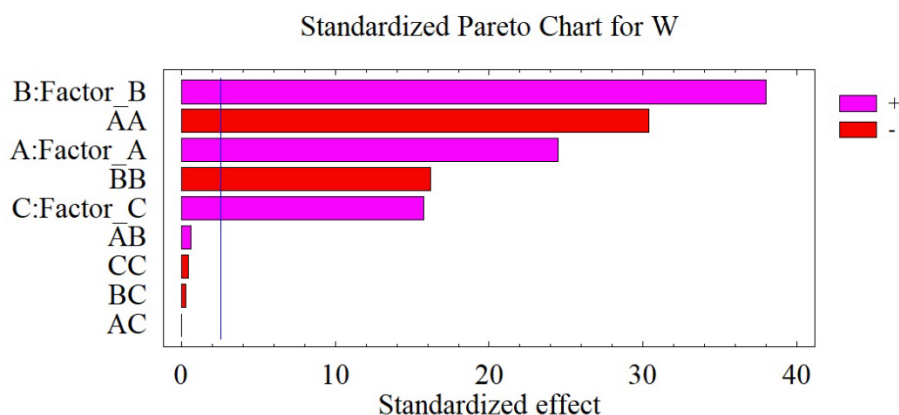


Fig. 2. Pareto map of model coefficients

The most significant effect on the dewatering of coal tar emulsion is exerted by the variable of the specific consumption of the demulsifier, which contributes to an increase in the target function. Among the individual variables, the second most important effect on the thermochemical dewatering of coal tar emulsion is the content of the "OS-25" in the demulsifying composition, and the lower effect is the content of ethanol in the water-alcohol mixture. The coefficients at the squares of the variables X_1^2 , X_2^2 the route of which corresponds to a decrease in dewatering, are of high significance. This may indicate the presence of optimal values for variables X_1 , X_2 . Other combinations of factors are not statistically significant.

The regression equation is presented in the form of a polynomial of the second degree, and taking into account the significance of the coefficients, it has the form:

$$W = 9,04 + 1,58875 \times X_1 + 2,465 \times X_2 + 1,02125 \times X_3 - 2,89917 \times X_1^2 - 1,54667 \times X_2^2$$

The adequacy of the obtained model of the process of thermochemical coal tar dewatering using a composite demulsifier is confirmed by the high value of the coefficient of determination $R^2 = 99.5903\%$, as well as by the small value of the standard error $SE = 0.183435$. The correspondence between the experimental and calculated data is illustrated in Fig. 3.

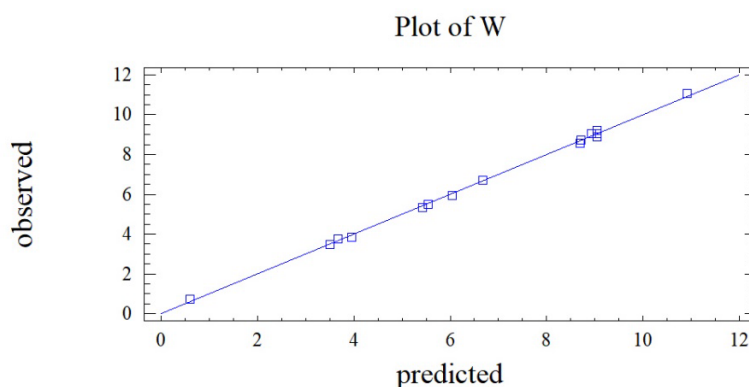


Fig. 3. Graph of comparison of observed and predicted values of the criterion function

As it follows from Fig. 3 in most cases the difference between the data is small and most of the experimental points are located near a straight line.

A three-dimensional graph of the dependence of the criterion function W from factors X_1 and X_2 is shown in Fig. 4, and contour graph is shown in Fig. 5. The less significant factor X_3 , which linearly increases the decrease in the moisture content in the coal emulsion, is fixed at zero.

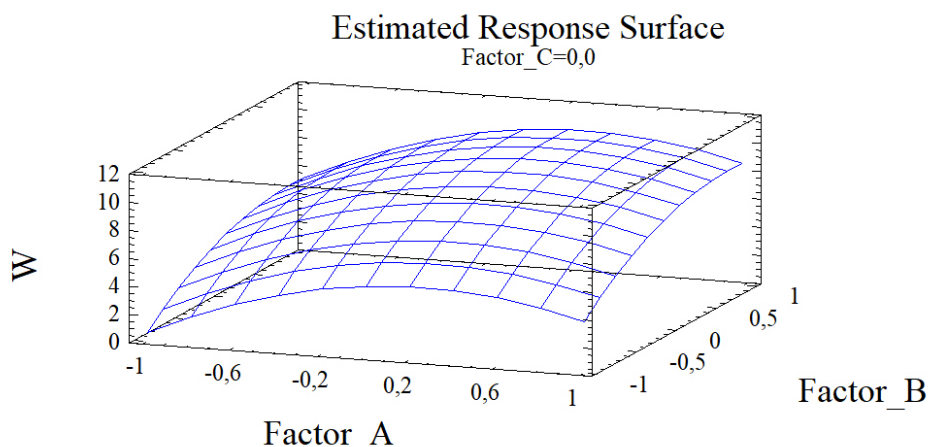


Fig. 4. Three-dimensional graph of the dependence of the absolute decrease in the moisture content of the coal tar emulsion (W , %) after contact with the demulsifying composition, depending on the content of OS-25 in the composition (factor A) and the consumption of the demulsifier (factor B)

As can be seen from the three-dimensional sections of the hypersurface (W) and the contour curves of these surfaces, the thermochemical dewatering of heavy coal tar increases with the consumption of the demulsifier and the ethanol content in the solvent of 5% concentration. From Fig. 4 it follows that an increase in the content of "OS-25" in a mixture with "PM 1441" promotes dewatering up to a certain limit, a further increase in the content of "OS-25" decreases the efficiency of the process under experiment condition. A more significant increase in dewatering is achieved by increasing the consumption of demulsifier. However, above a certain value, the introduction of an additional amount of demulsifier practically does not affect the thermochemical dewatering. This corresponds to the classical concepts of the effect of the consumption of demulsifier in the selected range on the dewatering of emulsions.

A less influencing factor is the ratio between the content of the universal reagent "OS-25" (wetting agent and detergent) and the content of the base reagent ("PM 1441"). At the same time, "OS-25" helps to remove coke and coal particles, but, mainly, more hydrophobic condensed aromatic dispersed toluene insoluble, for which naphthalene was taken as a model substance.

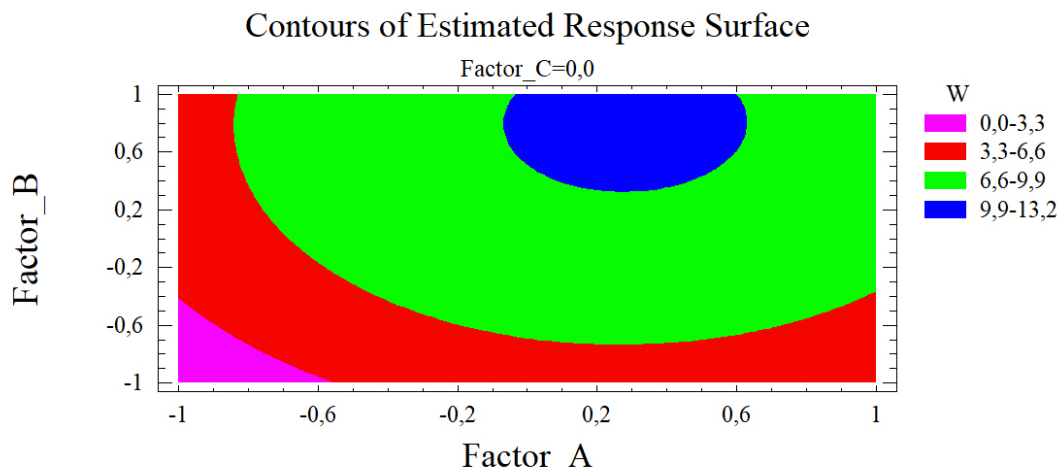


Fig. 5. Graph of contours of response surface

The area of maximum efficiency of the process (Fig. 5) is achieved at values $X_1 = 0,27$ and $X_2 = 0,75$. Taking into account the linear nature of the influence of factor X_3 on the process and in natural terms of values, the greatest dewatering of the coal tar emulsion is achieved at a demulsifier dosage of 225 g/t with an active substance content ("OS-25" 68% and "PM 1441" 32%), and at dissolving this composition in of in technical ethanol (5% solution).

Thus, the separation efficiency of water-tar emulsions based on heavy coal tar was increased by giving polyfunctionality to the composition prepared on the basis of the non-ionic demulsifier of domestic production "PM-1441". The decrease in the effectiveness of this reagent, most likely, was due to the strengthening of the armor shell around the dispersed water droplets in the heavy tar. Presumably, there was an increase in the hydrophobicity of dispersed particles insoluble in toluene, which is associated with an increase in their content in coal tar 3-4 times. Such an increase in hydrophobicity could occur due to their self-aggregation, while intermolecular interactions arose between the functional groups, which lowered the polarity of the formed aggregates. Such aggregates, closed on themselves by functional groups, have lost the ability to wet due to a decrease in polarity.

Therefore, composite demulsifying compositions are more effective and versatile reagents, since they have a wide range of surfactant properties and can be used for rheologically complex emulsions of coal tar, stabilized by an increased content of dispersed substances insoluble in toluene, as well as dispersed particles of coal, semi-coke and coke dust.

4. Conclusion

The chosen approach for the development of compositions for the separation of oil emulsions turned out to be fundamentally suitable for the preparation of a composite reagent intended for the breaking of emulsions based on highly pyrolyzed coal tar. A composition has been developed on the basis of a nonionic demulsifier "PM-1441 oil-soluble" and ethoxylated alcohol "OS-25" in a mass ratio of 32/68 for dissolving the active substance in a 5% solvent based on ethyl alcohol. The specified composition allows more efficient dewatering of coal tar with a high degree of pyrolysis than when using the base reagent "PM 1441".

The expediency of introducing a universal wetting and detergent reagent into the demulsifying composition indirectly confirms the assumption that a decrease in the effectiveness of the basic nonionic reagent during dehydration of heavier coal tar is associated with an increase in the hydrophobicity of blocked substances on the tar-water interface. This phenomenon can be explained by the tendency to self-aggregation of dispersed quinoline-insoluble substances with an increase in their concentration in the tar with a high degree of pyrolysis.

The limited range of cheap domestic-made surfactants narrows the area of using individual detergents and wetting reagents. Despite this, this method makes it possible to change the hydrophilicity of the demulsifier, its wetting and washing characteristics, and to modify the

base reagent when the nature of the dust entrainment from the coking chamber changes and in the case of a change in the degree of pyrolysis of the coal tar.

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