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EVALUATION OF DEMULSIFIERS EFFICIENCY FOR COAL TAR DEHYDRATION ACCORDING TO THE VALUE OF ITS VISCOSITY REDUCTION

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For the first time, the relationship between the efficiency of dehydration and the value of reducing the viscosity of the coal tar by adding demulsifier has been studied for "water in tar" emulsions. The dewatering of coal tar emulsions was investigated using 12 demulsifiers with different relative water solubility indices (RSN = 8.2–14.5) for tars of different pyrolysis grades. The effect of a series of demulsifiers on the viscosity of the dispersion medium of "water-in-tar" emulsions was studied. A low-pyrolysis tar was taken as a model of dispersion medium of emulsions with 1.2 % moisture content and 1.0 % of quinoline insoluble substances. A bottle test was used for a comparative evaluation of the demulsifying activity. The rheological characteristics of the studied tars were determined with a rotational controlled-shear rate rheometer Brookfield DV2T in a temperature range between 30 and 65 °C. When demulsifiers were added to the tar and the mixture was aged for 24 h, a decrease in viscosity was observed. When measured without withstanding, the viscosity of the mixture decreases in some cases only at a sufficiently high heating temperature (58 °C). The comparison of the dewatering efficiency with the mixture viscosity at 58 °C shows a linear dependence: the more the tar viscosity decreases when the demulsifier is added, the higher the dewatering efficiency when using this demulsifier for tars of different pyrolytic degree. Decreasing the viscosity of the tar promotes the coalescence of water drops and the diffusion rate of the demulsifier through the dispersion medium to the water-tar interface, which increases the efficiency of dewatering. The selectivity of tar dehydration by the studied demulsifiers is preserved for both low- and high-pyrolyzed coal tars. In the area of low viscosity reduction of the dispersion medium, the role of RSN is considerably higher, and an increase in the hydrophilicity of the reagent contributes to better dehydration. This may be due to the increased wetting ability of demulsifiers concerning emulsion stabilizers.

***Keywords**: coal tar, emulsion, demulsifier, viscosity, relative water solubility index*

INTRODUCTION

Coal tar is an important product of coal charge coking, the quality and yield of which depend on the raw materials and technological factors of its production [1–3]. Coal tar is a viscous multi-component polyeutectic and dispersed system, in which colloidal submicron and micron spheres of quinoline-insoluble particles, as well as droplets of water, the smallest particles of coke, coal and minerals are distributed [4–6]. Processing of coal tar involves its dewatering to 3–4 %, which is problematic, especially in the processing of viscous and heavy tars. To accelerate dewatering, coke plants use demulsifiers [7], although specially designed reagents for coal tar dewatering are not produced. Moreover, permanent use of any single demulsifying composition is hardly possible because the nature of stabilization of coal tar emulsion is changeable, and depends on coking conditions, class and type of coal and coke solids, water salinity, and other conditions of emulsion formation.

To date, the only way to select an appropriate reagent for coal tar dewatering is to test a wide range of available petroleum demulsifiers. In practice, this problem is solved using a "bottle test" [8], which is a problematic and time-consuming method. Determination of realizing water is complicated by lack of a clear boundary, flotation of coal tar in the surface water layer, formation of microemulsions in the water phase, and presence of large water inclusions in settling tar (entrained water). This reduces the accuracy of dewatering efficiency evaluation, especially for small volumes of emulsion under test. Therefore, the search for other ways of efficient evaluation of demulsifying compositions is an urgent and sudden increase of stability of tar emulsions at by-product coke plants requires new express methods for rapid screening of suitable demulsifiers. In addition, alternative persistence testing methods can help to reveal the nature of emulsion stabilization and help to improve demulsification efficiency or in some cases prevent the formation of persistent emulsions.

Numerous approaches are available to select emulsion breakers for various petroleum oils based on the basic principles of thermochemical emulsion breaking. In some cases, the applicability of demulsifiers can be evaluated by the molecular weight which is directly proportional to the efficiency of the demulsification [9]. This and similar characteristics of demulsifiers are also correlated to the nature of the basic reagent, the number of ethylene oxide – propylene oxide (EO/PO) blocks, RSN, *etc*. [10]. Increasing the separation efficiency of coal tar emulsions seems to be connected with the specificity of a particular emulsion, and the above-mentioned characteristics, although useful, can only serve as a starting point in the selection of a reagent in a particular case. Consideration of the specificity of a particular emulsion can be based on the main features of its destruction. As indicated in [11], the presence of a surface-active demulsifier can affect the emulsion in two ways – to change the rheology of the dispersion medium and induce flocculation of droplets by founding bridges between the droplets.

The selection of a suitable demulsifier for breaking oil emulsions is most often based on determining the surface tension of an oil-soluble demulsifier in oil, or a water-soluble one in water [12]. The most efficient are those reagents which significantly reduce the interfacial tension at low concentrations of surfactant. Lowering surface tension at the interface is one of the main requirements for demulsifiers. However, lowering the interfacial surface tension is not always a sign of superior demulsification activity of demulsifiers, the nature of the demulsifiers (structure and purity of the surfactant) also has an influence [13]. For example, an increase in dewatering occurs when more branched demulsifier molecules are used [14]. The demulsifier has to adsorb on the interfacial surface and displace the stabilizers, which block droplet coalescence, and reduce the surface tension between the hydrocarbon and aqueous phases and promote droplet coalescence [15]. In this case, the greatest surface activity has those reagents which have limited solubility at the interface, in this case in the dispersion phase - coal tar, and in the dispersion phase - water [16]. The predominant affinity of the demulsifier to the aqueous or organic phase is the basis for classifying the reagents according to the "relative solubility number" (RSN), which is a practical alternative to the hydrophilic-lipophilic balance (HLB) method [14, 17].

An equally important requirement for a demulsifier is the capability to penetrate the tar-water interface, which is also used in the selection of a suitable reagent. It is known that the dependence of viscosity on the dose of demulsifier is extreme and the minimum of the dynamic oil viscosity corresponds to the optimal dose of demulsifier [18]. Different surfactants reduce the viscosity of an emulsion to different degrees [19]. Non-ionic surfactants have been used successfully for the dehydration of coal tar [20, 21] and oil [16] which is consistent with investigations of the rheological behaviour of oil when different classes of demulsifiers are added. It turns out that the decrease in the viscosity of crude oil by adding non-ionic surfactants is deeper than by adding anionic and amphoteric surfactants [22]. Reducing the viscosity of the continuous phase is especially necessary for heavy tars with a high degree of pyrolization, which has a higher molecular weight. Such tars have reduced flowability and poor water separation because the high viscosity of the dispersion medium prevents the coalescence of water droplets. In addition, increasing oil viscosity increases emulsion stability due to the formation of an elastic layer of resins and asphaltenes around the phase contact boundary [23], and oil viscosity significantly increases due to the formation of asphaltene aggregates involving heteroatoms [24]. According to studies [25], when emulsion formation is artificial, as the viscosity of the solid phase increases, the average size of emulsion droplets decreases, and hence the persistence of such emulsions increases [16]. In contrast, when demulsifiers are added, emulsion viscosity decreases and water droplet size increases in the water-oil system [26].

A review of certain methods of selection of emulsifiers for persistent emulsions breaking as applied to the "water in coal tar" system shows that for rapid assessment of the suitability of demulsifier for breaking of coal tar emulsions, determination of dynamic viscosity of coal tar in a mixture with demulsifier is a simple and suitable way and takes into account features of the investigated coal tar. In this case, it is advisable to pay attention to the influence of demulsifier characteristics, e.g. with the RSN-index which is specified by individual demulsifier manufacturers. As for the coal tar and its fractions, there is a linear, unidirectional increase of viscosity and surface tension with increasing molecular weight [27], it can be assumed that the decrease of surface tension and viscosity at the application of the demulsifier in the coal tar will sufficiently predict the effectiveness of the demulsifier.

EXPERIMENTAL

To investigate the viscosity of coal tar with the addition of demulsifiers, a low pyrolysis (R1) tar with a minimum content of solid and liquid dispersion was taken. The reduction of water content in this sample was carried out by laboratory centrifugation. Tars of medium (R2) and high (R3-R4) pyrolysis degree were used only for the artificial preparation of watered emulsions to test the effectiveness of demulsifiers. Characteristics of the tars are shown in Table 1. The quality parameters of the tars were determined by standardized methods of property analysis by TU U 19.1-00190443-100: 2016.

Table 1. Characteristics of testing tars

Indices		R1	R2	R3	R4
Density at 20 °C, kg/m^3		1155	1197	1261	1280
Mass fraction of water, %		1.2	2.6	11.2	18.4
Mass fraction of substances, %:	**insoluble in toluene**	7.8	9.8	20	24.2
	insoluble in quinoline	1.00	5.8	18.7	20.9
	ash substances	0.10	0.10	0.15	0.16
The yield of distillation product from coal tars, mass fraction					
< 180 °C		2.22	1.5	1.2	0.74
180–200 °C		0.8	0.62	0.38	0.24
200–230 °C		19.32	15.9	11.6	9.4
230–300 °C		11.7	9.4	6.6	5.5
300–360°C		11.16	12.28	12.6	13.05
>360 °C		54.8	60.3	67.62	71.07

The presented samples of tars characterize the range of their quality change under the conditions of high-temperature coking at a comparable average temperature in the heating channels. Coal tar R1 was obtained at the most fully loaded coking chamber, and tars R3, R4 were produced at a significant underloading of chambers. With an increase in the degree of pyrolysis of the volatile coking products, tar density and viscosity increase, and the yield of oils during distillation (up to 360 °C) decreases. The R1 tar is characterized by low density, it settles well from water and ash, contains more phenols, has a lower yield of distillation residue, and also contains minimal amounts of dispersed solids, which are insoluble in quinoline. Therefore, the R1 tar is chosen as an analogue of the water-in-coal tar emulsion dispersion medium. Heavier tar samples (R2–R4) are not suitable for this task because they are less dehydrated and less ash-free. If such emulsions are exposed to the emulsifier when the dynamic viscosity is measured with a rotary viscosimeter, the emulsions may break and the rheometer will lose its value. In addition, the viscosity of coal tar emulsion is characterized by the extent of its watering, the content of substances insoluble in quinoline and their grain size distribution [28]. Thus, a comparison of the diffusive properties of demulsifiers and their capability to lower the viscosity of coal tar was carried out only on R1 tar. The demulsifying compositions from components of Clariant Oil Services (Switzerland) were prepared for tar dewatering experiments (Table 2).

Table 2. Demulsifying compositions

Component	Composition number										
	N 1	**N 2**	**N 3**	**N 4**	**N 5**	**N 6**	**N 7**	**N 8**	**N 9**	**N 10**	**N 11**
Dissolvan #3245	50	40	40	40	40	40	30	40	40	40	20
Dissolvan #5022		10									
Dissolvan #3879			10								
Dissolvan #3966				10							
Dissolvan #4006					10						
Dissolvan #5252						10	10				
Dissolvan #5022							10				
Dissolvan #3279								10			
Dissolvan # 4411									10	10	20
Isopropanol	10	10	10	10	10	10	10	10	10		10
Solvent	40	40	40	40	40	40	40	40	40	40	40
Methanol										10	10
Relative solubility number (calculated)	9.0	8.5	8.2	9.5	11.2	11.0	10.5	10.8	11.2	11.2	14.5

The compositions were chosen based on the assumption that the addition of demulsifiers with high and low RSN values to the basic demulsifier Dissolvan 3245 (RSN = 9), which has a medium affinity to the dispersion phase of the emulsion, can improve the efficiency of emulsion breaking. In the first case, this would be due to the high wetting ability of a reagent with a high RSN value. In the last case suggested improvement would be due to the increased affinity of the demulsifier to the more hydrophobic heavier coal tar. The characteristics of the demulsifiers are shown in Table 3.

Table 3. The characteristics of the main components used for the preparation of demulsifiers

Name of dissolvan	Relative solubility number	Mass fraction of active substance, %	Water solubility (20 °C)	Density at 20 °C (DIN 51757), g/cm^3	Dynamic viscosity at 20 ºC (DIN 53015), mPa·S
3245	9.0	100	soluble, turbid	1.03	10000
5022	6.5	100	insoluble	1.00	4000
3879	4.0	80	forms a gel	1.01	2000
3966	12.5	70	insoluble	1.02	21000
4006	22.1	80	miscible, phase separation	1.05	8000
5252	19.0	100	soluble	1.04	1300
3279	20.5	72	insoluble	1.04	5500
4411	20.0	100	soluble	0.95	25

The main active components used for the preparation of demulsifiers are as follows: Dissolvan 3245 - cross-linked oxypropylated PO/EO-block polymer ($C_{15}H_{16}O_2$-C_3H_6O-C_3H_5ClO-C_2H_4O)$_x$, phenol, 4,4′-(1-methylethylidene) bis-; polymer with 2-(chloromethyl)oxirane; 2-methyl oxirane; oxirane; Dissolvan 5022 - amino alkoxylate (oxypropylated polyamine); Dissolvan 3879 - polyester; Dissolvan 3966 - oxyalkylated (oxyethylated) resin; Dissolvan 4006 - oxyalkylated (oxyethylated) resin; Dissolvan 5252 - oxyethylated PO/EO-block polymer $(C_4H_{11}NO_3\text{-}C_3H_6O\text{-}C_2H_4O)_x$, 1,3-Propanediol, 2-amino-2-(hydroxymethyl)-; polymer with 2-methyl oxirane; oxirane; Dissolvan 3279 - oxyalkylated (oxyethylated) resin in high boiling hydrocarbons solvent; Dissolvan 4411 - ethylene/propylene oxide dissolved in methanol. As a comparison demulsifier of non-ionic type PM 1441 (JSC Fine organic synthesis plant "Barva", (Ukraine) was used, that was a solution of a block copolymer of ethylene oxide and propylene oxide, which is regularly used at Ukrainian coking enterprises.

"Bottle test" was used for comparative evaluation of demulsifying activity, which had been introduced as an internal standard in oil production companies. The basic principles of this comparative testing of demulsifier efficiency were formulated in [29]. To comply with them (selection of a representative sample, sampling only fresh samples, the same mixing conditions and maximum identity of sampling) the following methodology was used. The model emulsions were prepared by effective mixing of the fresh coal tar and distilled water in the required proportion and thermostated for 1 h at the required temperature. The resulting emulsion was stable at least for 96 h. It was previously found that to obtain a comparable performance under these conditions, the amount of water in the individually prepared emulsions should be in the range of ≈ 25–30 %. Plastic bottles (0.5 dm^3) were used as laboratory water tanks. Initially, reagents in the form of 5 % solutions (or dispersions) were introduced into the bottles, the dosage was 200 ppm. An equivalent amount of distilled water was added to the blank sample instead of demulsifying compositions. After the adding of emulsions with a mass of 400 g into the bottles, the latter was stirred manually with the same number of shakes and with the same intensity. Then the series of bottles were placed simultaneously in a thermostat at a set temperature of 60 °C for three hours. At the end of the experiment, released water was carefully decanted and weighted to an accuracy of 0.01 g, and the amount of residual water in the coal tar emulsion was determined according to the normative documents (TU U 19.1-00190443-100: 2016).

The rheological characteristics of the studied tars were determined with a rotational controlled-shear rate rheometer Brookfield DV2T in a temperature range between 30 and 65 °C. Viscous flow tests were carried out in a shear rate range of 1.2–250 s^{-1} using Searle geometry. The essence of the method is to record the moment of resistance of an inner cylinder with the fluid under test at different shear rate gradients and to calculate the shear stress and dynamic viscosity. At least five replicates of each test were performed on fresh samples.

The efficiency of demulsifying compositions was assessed by the formula:

$$E = (W_1 - W_2)\times 100/W_1,\ \%, \qquad (1)$$

where W_1 is the initial water content in coal tar emulsion, W_2 – water content in treated emulsion after the experiment.

RESULTS AND DISCUSSION

The results of measuring the viscosity of the R1 tar are shown as a graphical relationship to the shear rate at different temperatures in Fig. 1.

With the increasing temperature up to 58–65 °C, flow aggregates decompose and the dynamic viscosity of R1 tar practically does not depend on shear rate and acquires Newtonian flow character. The such character was not obtained in the all-remaining tar samples R2-R4, probably due to the presence of the dispersed phase and the more complex nature of the interaction of substances with a higher molecular weight. Therefore, tar sample R1 was chosen to measure the viscosity of the tar when a demulsifier was added, and measurements were made at a shear rate ensuring a Newtonian flow character (220.1 s^{-1}). The search for correlation of the influence of demulsifiers on tar viscosity was carried out in the temperature range close to conditions of tar decanting in plant and laboratory conditions. To view the dynamics of the interaction of reagents, viscosity measurements have been made immediately after spreading and mixing of demulsifier with tar and after 24 h of ageing. The results of the measurements are presented in Table 4.

As it follows from the measurement results, a decrease in the viscosity of the mixture is observed when the demulsifiers are added and the mixture is incubated for 24 h, which agrees with the data [18, 26], which is explained by a change in the rheology of the dispersion medium [11]. It has been found that after addition of a demulsifier in the emulsion there is a decrease in apparent viscosity for an emulsion, with the same water content [11]. In our case, however, the dispersion medium was modeled off a tar with a low content of water and dispersed solids. Different demulsifiers decrease the viscosity of the original tar in different ways, which prove the influence of the nature of the demulsifier on tar flow. When measured without keeping, the viscosity of the mixture decreases only at a sufficiently high heating temperature (58 °C); at lower temperatures for the three demulsifiers, a slight increase of 0.4–1.6 mPa·S in viscosity was observed. This data already shows that to compare the efficiency of the reagents action, it is necessary to keep the tar with the reagent for one day and heat it to 58 °C to make the tar flow with Newtonian character.

Table 4. The viscosity of R1 tar, treated by demulsifier's compositions, mPa·S

Medium	Measurement immediately after mixing at temperature, °C			Measurement after 24 h at temperature, °C		
	58	**44**	**36**	**58**	**44**	**36**
Coal tar R1	11.79	17.47	30.47	11.79	17.47	30.47
R1 + #1	10.51	15.07	26.63	8.31	15.18	26.15
R1 +#2	9.81	18.34	31.49	9.15	15.08	26.72
R1 +#3	8.90	14.83	29.85	8.71	14.18	17.08
R1 +#4	9.72	17.91	24.43	6.83	16.21	22.78
R1 +#5	11.59	15.40	23.30	8.92	12.52	20.67
R1 +#6	9.75	16.42	29.13	8.00	14.5	24.56
R1 +#7	8.52	15.38	27.52	7.89	11.95	18.42
R1 +#8	11.34	16.27	30.18	7.18	15.25	18.75
R1 +#9	8.57	18.3	32.03	6.85	11.75	19.2
R1 +#10	7.56	16.58	26.83	6.81	15.38	25.42
R1 +#11	7.73	16.14	26.03	7.62	15.79	25.93
R1+PM 1441	9.80	16.52	28.50	8.2	14.00	24.00

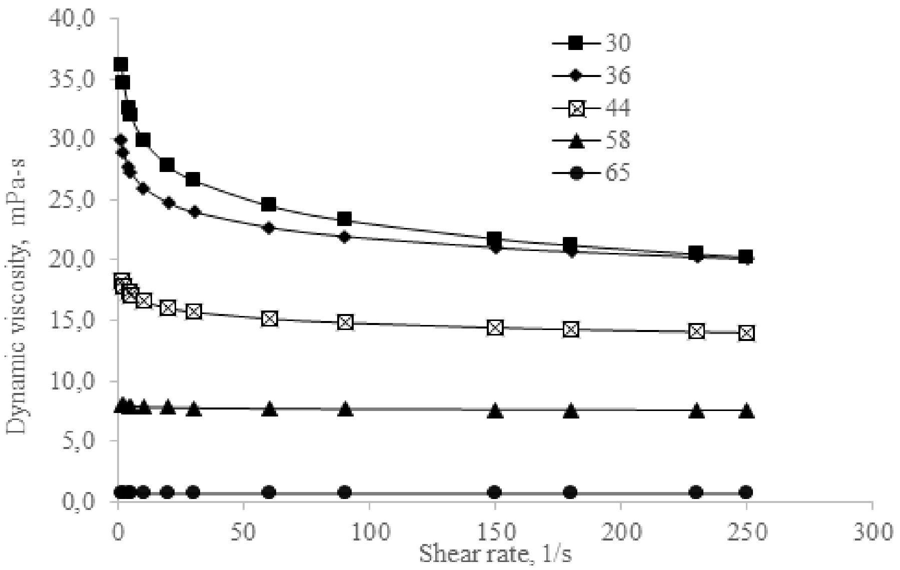

Fig. 1. Flow curves of R1 tar at different test temperatures

Table 5. Efficiencies of de-watering of coal tars with the addition of demulsifiers, %

Reagent	Coal tar:			
	R1	R2	R3	R4
#1	8.6	12.0	14.0	53.6
#2	0.0	18.7	30.0	52.6
#3	0.0	13.3	30.0	66.8
#4	57.1	86.7	68.0	88.3
#5	21.4	56.0	44.0	78.5
#6	94.3	60.0	60.0	79.8
#7	57.1	60.0	45.0	72.7
#8	68.6	69.3	64.0	92.0
#9	62.9	66.7	64.0	82.5
#10	65.7	80.0	59.0	77.7
#11	34.3	86.7	45.0	68.0
PM 1441	28.6	76.7	54.0	73.7

The effect of demulsifiers on emulsion separation has been evaluated on artificially watered R1-R4 tars using “bottle tests”. The results of tar dehydration with demulsifying compositions (Tables 2–3) are presented in Table 5.

Comparison of obtained dehydration efficiency with tar R1 viscosity at 58 °C shows a linear dependence (Table 6): the more the tar viscosity decreases at demulsifier injection, the higher the dehydration efficiency at this demulsifier for tars of different pyrolytic grade R1-R4.

There is no similar correlation for other temperature measuring conditions; a lower coefficient of determination is observed for the tar viscosity values immediately after the demulsifier adding at 58 °C.

Table 6. Determination coefficient (R^2) of the linear dependence of efficiency of different coal tars dewatering on tar viscosity

Determination coefficient	Coal tar:			
	R1	R2	R3	R4
R^2	0.53	0.52	0.55	0.46

The observed decrease of the tar viscosity after demulsifier addition seems to be a consequence of further destruction of structured flow units which distort the Newtonian character of the flow. The decrease of the tar viscosity facilitates diffusion of the demulsifier through the dispersion medium to the “water-tar” interface, which raises the efficiency of dewatering. The selectivity of tar de-watering by the studied demulsifiers is preserved for both low- and high-pyrolyzed tars. Despite the complexity of the structure of high-pyrolyzed tar, which forms a disperse system of “tar-quinoline insoluble particles”, “tar-solid particles” and “tar-water droplets”, the capability of the demulsifier to penetrate through the dispersion medium to water droplets is similar for light and heavy tars. It is known that the efficiency of dewatering deteriorates with an increase in density of the coal tar. From the results obtained it may be assumed that this deterioration is caused by an increase in the content of inclusions in the dispersion medium and not by an increase in the molecular weight. It seems to be the dispersed medium impedes dewatering rather than the continuous phase viscosity increase.

Yet the low values of the coefficient of determination show only a partial effect of the dispersion medium viscosity on the efficiency of dewatering with demulsifiers and the presence of additional factors. It is necessary to take into account the influence of the nature of the demulsifier on the armouring layer. In particular, the affinity of the demulsifier for emulsion stabilizers is characterized by its index of relative solubility in water (RSN). For demulsifiers N 1–11 the calculated values of the index of relative solubility in water are presented in Table 2, which is known to be the measure of hydrophilicity of reagents and characterizes wetting capability. The obtained data of dewatering efficiency (Table 5) are processed by the multiple regression method, the efficiency of tar dewatering with the help of a demulsifier is expressed by the following equation:

$$Z = a + b \times X^{n1} + c \times Y^{n2} + d \times (X \times Y)^{n3} \qquad (2)$$

where *a*, *b*, *c*, and *d* are coefficients of the equation (2), n_1, n_2, and n_3 are power factors; *X* is the viscosity of the tar when adding the demulsifier (58 °C) and 24 h exposure time, mPa·S, *Y* is the index of relative solubility of demulsifier in water (RSN). Parameters of equation (2) are given in Table 7.

Table 7. Multiple regression equation coefficients and coefficients of determination (R^2) for tars of various degrees of pyrolysis

Parameters	Coal tar:			
	R1	**R2**	**R3**	**R4**
a	692.5479	-1075.55	-254.121	2042.714
b	-0.02863	4976.103	9826.126	-1367.54
c	-0.06575	-84.0422	-0.93224	-6.87707
d	-10184.4	5.1	3.0	2.6
n_1	4	-0.7	-2	0.2
n_2	3	0.9	2	1.5
n_3	-0.71	1.1	1	1.1
R^2	0.810	0.916	0.750	0.716

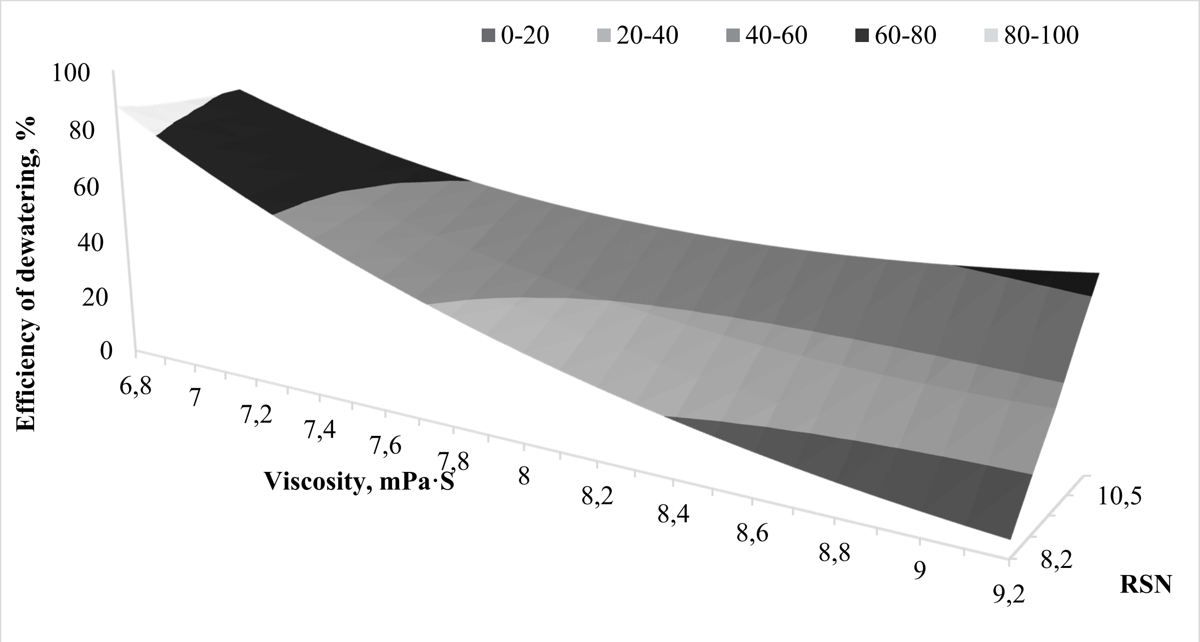

Fig. 2. Tar R2 dewatering efficiency plotted from regression equation (2)

The maximum coefficient of determination was obtained for the medium pyrolysed tar R2; for this system, the effect of the studied factors on the dewatering efficiency is shown in Fig. 2.

According to Fig. 2, a deeper reduction in the viscosity of the tar when adding a demulsifier corresponds to higher efficiency of dewatering, in which case the impact of the RSN reagent is not so significant. For more viscous media, the effect of RSN reagent is greater, as the hydrophilicity of the reagent increases, the dewatering efficiency also increases.

CONCLUSIONS

Evaluation of the effectiveness of demulsifiers for coal tar dehydration by the value of the viscosity reduction can be performed by making the dispersion medium Newtonian flow character, for which the exposure of demulsifiers with dehydrated and deashed tar for a day and at heating to 58 °C was applied.

For the studied reagents, the decrease in viscosity due to the action of the demulsifier contributes to the efficiency of dehydration more than the effect of the relative water solubility index. This reduction occurs in tars with varying degrees of pyrolysis, the capability of the reagent-demulsifier to penetrate through the dispersion medium to the water droplets has a similar character for light and heavy tars under these conditions.

In the area of a small decrease in the viscosity of the dispersion medium, the role of RSN is significantly higher, increasing the hydrophilicity of the reagent contributes to improved dehydration. This may be related to the increased wetting capability of demulsifiers with respect to emulsion stabilizers. The data obtained confirm the assumption that the determining factor of tar dehydration is the capability of the demulsifier to weaken the intermolecular interaction between flow units, which improves conditions for coalescence of droplets and increases conditions for the reagent to penetrate through the dispersion medium to the phase interface.

Increasing the role of RSN reagent on dehydration is shown when its capability to decrease the viscosity of the dispersion medium is low, the reagent efficiency is minimal when its inability to decrease the viscosity of the dispersion medium and not to wet the emulsion stabilizers.

Increasing the index of relative solubility in water reagent probably contributes to wetting of hydrophobic emulsion stabilizers and especially improves the efficiency of dewatering when using demulsifiers weakly reducing the viscosity of the tar.

Оцінка ефективності деемульгаторів для зневоднення кам’яновугільних смол за величиною зниження їхньої в’язкості

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Вперше для емульсій типу «вода в смолі» досліджено взаємозв’язок між ефективністю зневоднення та величиною зниження в’язкості кам’яновугільної смоли при додаванні деемульгаторів. Досліджено зневоднення емульсій кам’яновугільних смол з використанням 12 деемульгаторів з різними показниками відносної розчинності у воді (RSN = 8.2–14.5) для смол різних пірολізних марок. Вивчено вплив ряду деемульгаторів на в’язкість дисперсійного середовища емульсій «вода в смолі». Як модель дисперсійного середовища емульсій була взята смола низького ступеня піролізу з вмістом вологи 1.2 % і нерозчинних речовин в хіноліні 1 %. Для порівняльної оцінки деемульгуючої активності використали bottletest. Реологічні характеристики вивчених смол були визначені з ротаційним реометром з контрольованою швидкістю зсуву Brookfield DV2T в температурному діапазоні між 30 і 65 °C. При додаванні деемульгаторів в смолу та витримці суміші протягом 24 год спостерігається зниження в’язкості. При вимірюваннях без витримки в’язкість суміші знижується лише за досить високої температури нагрівання (58 °C). Порівняння ефективності зневоднення *з в'язкістю суміші при 58 °С показало наявність лінійної залежності: чим більше знижується в'язкість смоли при введенні деемульгатора, тим вище ефективність зневоднення при використанні цього деемульгатора, причому для смол різного ступеня піролізованості. Зниження в'язкості смоли сприяє коалесценсії крапель води та дифузії деемульгатора крізь дисперсійне середовище до межі розділу фаз, що підвищує ефективність зневоднення. Вибірковість зневоднення смоли дослідженими деемульгаторами зберігається для смол як низького ступеня піролізованості, так і високої. В області малого зниження в'язкості дисперсійного середовища роль RSN істотно вища, збільшення гідрофільності реагента сприяє поліпшенню зневоднення. Це може бути пов'язано з підвищенням змочувальної здатності деемульгаторів по відношенню до стабілізаторів емульсій.*

***Ключові слова**: кам'яновугільна смола, емульсія, деемульгатор, в'язкість, індекс відносної розчинності у воді*

REFERENCES

1. Mukina N.V., Miroshnichenko D.V. Coking Stamped Coal Batch. 3. Yield of Chemical Products. *Coke Chem*. 2021. **64**(9): 397.
2. Fatenko S.V., Faenko S.Y., Bannikov L.P., Nesterenko S.V., Miroshnichenko D.V. Adjusting the Primary Cooling of Coke-Oven Gas for Batch with Elevated Gas-Coal Content. *Coke Chem*. 2020. **63**(4): 188.
3. Bannikov L.P., Miroshnichenko D.V., Nesterenko S.V., Balaeva Y.S., Fatenko S.V. Influence of Small Coal Particles in Coking Batch on Coal-Tar Quality. *Coke Chem*. 2019. **62**(3): 95.
4. Li J.H., Wei X.Y., Zhao H.F., Yan W.W., Teng D.G., Ma Z.H., Zong Z.M. Effective Separation of Condensed Arenes from High-Temperature Coal Tar and Insight into Related Intermolecular Interactions. *Energy Fuels*. 2021. **35**(5): 4267.
5. Deng S., Zhou J. An experimental study of the effect of water content on combustion of coal tar/water emulsion droplets. *Energy*. 2011. **36**(10): 6130.
6. Nazarov V.G. Removal of naphthalene and tar from coke–oven gas in primary cooling and condensation. *Coke Chem.* 2016. **59**(6): 221.
7. Liu J., Zhu Y., Miao Zh., Cui L., Liu J., Fan X., Du Ch., Dan Y., Teng H., Li D. Study on the Pretreatment Process and Removal Rules of Sulfur-Containing Compounds for Medium- and Low-Temperature Coal Tar. *ACS Omega*. 2021. **6**(19): 12541.
8. Yun S.H., Kim C., Kim Y.C., Lee E.S. Dewatering of Coal Tar by Heat Treatment. *Energy Fuels*. 1999. **13**(2): 459.
9. Zheng X., Ying Zh., Cui J., Wang B., Chen J., Zhang Q. Simultaneous dewatering and recovering oil from high viscosity oily sludge through the combination process of demulsification, viscosity reduction and centrifugation. *Energy Fuels*. 2017. **31**(12): 14401.
10. Kailey I., Blackwell C., Behles J. Effects of Crosslinking In Demulsifiers on Their Performance. *Can. J. Chem. Eng*. 2013. **91**(8): 1433.
11. Al-Sabagh A.M., Nasser N.M., Abd El-Hamid T.M. Investigation of Kinetic and Rheological Properties for the Demulsification Process. *Egypt. J. Pet*. 2013. **22**(1): 117.
12. Tao J., Shi P., Fang Sh., Li K., Zhang H., Duan M. Effect of Rheology Properties of Oil/Water Interface on Demulsification of Crude Oil Emulsions. *Ind. Eng. Chem. Res*. 2015. **54**(17): 4851.
13. Zolfaghari R., Abdullah L.C., Biak D.R.A., Radiman S. Cationic Surfactants for Demulsification of Produced Water from Alkaline−Surfactant−Polymer Flooding. *Energy Fuels.* 2019. **33**(1): 115.
14. Kailey I., Feng X. Influence of Structural Variations of Demulsifiers on their Performance. *Ind. Eng. Chem. Res.* 2013. **52**(2): 785.
15. Raya S.A., Saaid I.M., Ahmed A.A., Umar A.A. A critical review of development and demulsification mechanisms of crude oil emulsion in the petroleum industry. *J. Pet. Explor. Prod. Technol*. 2020. **10**: 1711.
16. Sakhabutdinov R.Z., Gubaidulin F.R., Ismagilov I.Kh., Kosmacheva T.F. *Peculiarities of formation and destruction of oil-water emulsions at a late stage of oil field development*. (Moscow: JSC VNIIOENG, 2005). [in Russian].
17. Wu J., Xu Y., Dabros T., Hamza H.A. Development of a Method for Measurement of Relative Solubility of Nonionic Surfactants. *Colloids Surf. A*. 2004. **232**(2–3): 229.
18. Tiwari M.P. Effects of Demulsifier on Dynamic Viscosity and Interfacial Tension for Governing Crude oil Demulsification. *Int. J. Recent Sci. Res*. 2019. **10**(09): 34791.

19. Yaghi B.M., Al-Bemani Y., Al-Bemani A. Heavy Crude Oil Viscosity Reduction for Pipeline Transportation. *Energy Sources*. 2002. **24**(2): 93.
20. Patent WO2016113987A1. Yangping P., Yoshikawa Y.T. Oil-water separation method for water-containing coal tar and oil-water separation agent. 2016.
21. Bannikov L.P. Selection of type and justification of methods of applying a demulsifier for breaking up coal tar inverse emulsions. *Journal of Coal Chemistry*. 2017. **1**: 31.
22. Liu M., Wu Y., Zhang L., Rong F., Yang Z. Mechanism of viscosity reduction in viscous crude oil with polyoxyethylene surfactant compound system. *Pet. Sci. Technol*. 2019. **37**(4): 409.
23. Goodarzi F., Zendehboudi S. A Comprehensive Review on Emulsions and Emulsion Stability in Chemical and Energy Industries. *Can. J. Chem. Eng*. 2019. **97**(1): 281.
24. Shi L., Liu Ch., Chen M., Hua Zh., Ye Zh., Zhang J. Synthesis and evaluation of a hyperbranched copolymer as viscosity reducer for offshore heavy oil. *J. Pet. Eng.* 2021. **196**(1): 108011.
25. Alliod O., Messager L., Fessi H., Dupin D., Charcosset C. Influence of viscosity for oil-in-water and water-in-oil nanoemulsions production by SPG premix membrane emulsification. *Chem. Eng. Res. Des*. 2019. **142**: 87.
26. Abdulredha M.M., Hussain S.A., Abdullah L.Ch. Separation Emulsion via Non-Ionic Surfactant: An Optimization. *Processes*. 2019. **7**(6): 382.
27. Zykov D.D., Pats B.M. *Naphthalene coke-chemical*. (Moscow: Metallurgia, 1981). [in Russian].
28. Bannikov L., Pasternak A., Pokhylko V., Pilipenko V. Rheological properties of washing emulsions for gas cooling systems. *Coke Chem.* 2015. **58**: 303.
29. Abdulkadi M. Comparative analysis of the effect of demulsifiers in the treatment of crude oil emulsion. *ARPN J. Eng. Appl. Sci*. 2010. **5**(6): 67.

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