

Modification of Water Washing of Coal Tar and its Potential to Reduce the Level of Quinoline Insoluble Substances

L. P. Bannikov¹, O. L. Borisenko¹, F. F. Cheshko¹, A. L. Bannikov²

¹ Ukrainian State Coal-Chemistry Institute (SE "UKHIN"), 61023, Kharkiv, 7 Vesnina Str., Ukraine

² National Technical University «Kharkiv Polytechnic Institute», 61002, Kharkiv, 2 Kirpichova Str., Ukraine

Received April 25, 2023; Accepted July 19, 2023

Abstract

The object of the study was a highly pyrolyzed coal tar, which contains too high a value of quinoline insoluble substances. This prevents its further processing into a high value-added product, the electrode pitch. There are many developments to reduce the quinoline insoluble content of heavy tar, although they are somewhat effective, they require the use of a centrifugal field, expensive solvents and the disposal of by-products. Our attention was drawn to a simple method of water washing of the tar, which can reduce the ash content of the tar, improve the dehydration of the tar and slightly reduce the quinoline insoluble content. It is hypothesised that surfactants will improve the efficiency of coal tar washing. For the solubilisation of dispersants insoluble in quinoline, surfactants with more than 16 HLB were chosen from the proxanol group and polyoxyethylene fatty alcohols. However, the best results for the reduction in quinoline insolubles did not exceed 2–3 % (absolute). Estimation of energy of intermolecular interaction between hydrophilic and hydrophobic parts of nonionic surfactant and model components of substances, insoluble in quinoline, showed the reason of low efficiency of solubilization. It lies in the comparability of the value of energy of intermolecular interaction of molecules included in quinoline insolubles with the energy of intermolecular interaction of these substances with the solubilizing agent.

Keywords: Coal tar; Quinoline insoluble substances; Washing; Surfactant; Intermolecular interaction.

1. Introduction

A high degree of pyrolyzation is the main obstacle to the stable distillation processing of coal tar at coke plants in Ukraine, which is characterised by local installations of low productivity or insufficient load on coal tar processing. As a rule, it causes small stock of coal tar storage for averaging of tar of different quality, so there is always demand for raw materials with narrow ranges of quality indicators [1-2].

The content of substances insoluble in quinoline is limited in the requirements for the electrode pitch produced during tar processing. Therefore, any technology that reduces the quinoline insoluble (QI) content even slightly is relevant and deserves detailed consideration.

Tar with a low QI content can be removed through a hydroseal of the primary gas cooler and then sent to mechanised clarification for final gravity sedimentation [3]. The disadvantage of this method is the low proportion of tar condensing in the primary gas cooler, its high water content and the need for an additional mechanised clarifier. Facilities for tar de-sludge removal, introduced in condensation departments of some Ukrainian coke plants, do not provide separation of dispersed particles insoluble in quinoline. Dimensions of these particles are in the range from 0–7,0 to 0–20 microns. Operation of tricanter removes 95 % of all particles larger than 71 µm, particle sizes smaller than 10 µm are not separated by centrifugation [4]. To intensify separation of QI, methods of aggregation of such particles at appropriate temperatures for enlargement and subsequent centrifugation [5-6] or multistage treatment of tar in centrifugal field [7] have been developed. However, such methods are very costly: aggregation

of micron-sized particles occurs during thermal aging of tar at 350°C, and several stages of centrifugation can be used only in obtaining products with high added value.

Technologies of deep removal of QI from coal tar are considered with the purpose of obtaining special grades of coal tar pitch (impregnated pitch, needle coke, carbon fibre, mesophase pitch, etc.). It is suggested to precipitate QI from coal tar in a centrifugal field with a preliminary dilution with absorption oil. For achievement of degree of extraction QI on 88–89 % at 4500 rpm the five-minute holding time of a mix containing 15 % of oil or 15-minute holding time with 9 % of absorbing oil is recommended [8]. Widely developed methods of QI extraction from coal tar is solvent extraction [9–11]. However, this method demands consumption of a considerable quantity of expensive reagents. It is considered that a combination of several methods is the most promising way to remove substances insoluble in quinoline from coal tar [12].

Earlier at the coke plants of Ukraine the operations of tar washing at tar-extraction installations were widely used. A by-product effect was reduction of water and ash content in washed tar, while there was a slight decrease in content of substances insoluble in toluene. In such settings was mixing tar with ammonia water in a paddle mixer in the volume ratio of 1:1, after which the resulting mixture was broken in a mechanized settling tank at 85–95°C for 10–15 hours. In these conditions the tar decreased in moisture from 6.7–7.9 % to 2.1–5.0 %, and substances insoluble in toluene from 6.4–7.9 to 6.2–7.5 % [13–14]. There is also evidence that the water content decreased from 7.4 to 3.4 % and the insoluble in toluene from 10.2 to 9.5 % under similar conditions [15].

Analysis of the data [16] shows that reducing the water /tar ratio from 1/1 to 1/3 in laboratory test conditions leads to an increase in the water content of the tar, while the insoluble content in toluene at the same time decreases. The absolute proportion of reduction in the latter case depends little on this ratio, the ash content of the tar and the type of washing fluid. The absolute share of reduction of insoluble content in toluene varies in a wide range (2–10 %) and on the average is 5.2 %. The actual maximum reduction of substances insoluble in toluene is 10.5 to 9.5%, which in terms of quinoline insoluble substances can be about 0.5–1.0%. The possible mechanism and conditions for increasing the degree of removal of insoluble in quinoline by tar washing are not covered in these works.

Washing with hot water is a simple and common method of breaking water-in-oil emulsions. At the same time salts and mechanical impurities are removed [16]. Thus, the processes of dehydration and partial removal of quinoline insoluble substances are interrelated, which is also confirmed by research conducted on coal tar [17].

It is rational to add surfactants to increase the removal of quinoline insoluble substances. Such studies have been conducted when additives are added to destabilize the system and intensify the precipitation without introducing wash water [17]. During 96 hours of gravity settling various fuel and fuel oil additives were added to tar samples with water content of 3.4–3.6 % in quantity of 2 %. The greatest effect was obtained for an additive with the trade name "AzNII": the reduction of QI content was from 4.5 to 2.5 % and from 6.2 to 4.1 %. The decrease in QI content in the blank sample during settling was 0.6–0.7%, which reduces the effect of additive injection. The content of insoluble in toluene increased in all samples during settling, which indicates the complex processes of redistribution of group composition during thermal aging of the tar. Obviously, this process involves the deposition of quinoline-insoluble aggregates, apparently enlarged under the action of surfactant, or the deposition of ash particles with adsorbed under the action of surfactant on ash particles of substances insoluble in quinoline. In either case, it is necessary to establish the distribution of QI over the height of the tar layer and to determine the yield of the tar volume with an appropriate degree of QI reduction. Pilot tests, however, have confirmed that the reduction of QI content is 2 % (absolute) with the yield of substandard products (top and bottom layers) of 8–10 % of the initial mass [18].

In our opinion, it is reasonable to test the method of dewatering and reduction of quinoline insoluble substances by water washing with surface-active reagents. This method makes it

possible to transfer ash particles with adsorbed substances insoluble in quinoline into an aqueous layer. This is confirmed by the practice of tar sedimentation in mechanized clarifiers: the reduction of ash content in the tar occurs when the aqueous layer is increased, i.e. by increasing the path of the tar drop in the water layer.

By an alternative mechanism, aqueous surfactant solutions can solubilise mechanical emulsion stabilisers, the resulting micelles then coagulate and the resulting structures become large enough for gravity deposition. Similar solubilization processes of polycyclic aromatic hydrocarbons were applied for highly hydrophobic tar components (fluorene, fluoranthene, pyrene, phenanthrene). It was shown that hydrocarbons with similar hydrophobic properties and melting points can compete for a similar place in the micelle. Moreover, as the number of solubilizers in the system increased, the total mass and volume of solubilized product increased [19–20]. This fact suggests that for a highly pyrolyzed tar with a higher content of substances insoluble in quinoline, the total mass of solubilized and subsequently released QI, will be higher than for low-pyrolyzed tars.

An additional confirmation of this hypothesis can be the complex mechanism of oil emulsion destruction, which involves softening of the asphaltene film at the oil–water interface, changing the interfacial mobility of asphaltenes [21]. As surfactants, demulsifiers help to push asphaltenes out of the interfacial surface of the emulsion [22]. Asphaltenes are insoluble in water even at elevated temperatures [23], but can be solubilised by surfactants to form supramolecular aggregates [24]. Analogous to the process in question is the chemical method of thermal washing (thermal desorption method), which is used to wash oil sludge with hot water and chemical reagents, resulting in oil, water and sludge [25].

2. Experimental

For research we took samples of coal tar, the quality properties of which were determined in accordance with TU U 19.1–00190443–100:2016 (Table 1).

Table 1. Characteristics of coal tar

Parameter	The value for the tar:	
	R1	R2
Density, kg/m ³	1212	1196
Water content, mass fraction, %	2.3	2.0
Mass fraction of toluene insoluble, %	12.1	10.0
Mass fraction of quinoline insoluble, %	8.3	5.8
Ash content, mass fraction, %	0.21	0.11
Naphthalene content, %	9.6	9.9
pH of aqueous extract	7.7	7.5

Selection of surfactants for water washing of coal tar was carried out based on the availability of reagents and on available data on the solubilization of high-molecular-weight components of coal tar. First, for this purpose it is convenient to use demulsifier "PM", which became popular to improve tar sedimentation at by-product coke enterprises of Ukraine [26–27]. In addition, for solubilization it is necessary to use surfactants with HLB number more than 16, in this case, a class of polyoxyethylene fatty alcohols proved to be good [28]. Tables 2–4 present the basic properties of surfactants used by the PJSC "Barva Fine Organic Synthesis Plant" for washing the tar with aqueous solutions.

Table 2. Characteristics of demulsifier "PM" aqueous solution

Parameter	Value
Clarification temperature of 10 % solution of demulsifier in 5 % NaCl solution, °C	50–60
Kinematic viscosity at 20°C, cSt	40–70
Mass fraction of active substance, %.	63–67
pH of 2 % aqueous solution	6–8
Solidification temperature, °C	–35

Table 3. Characteristics of the reagent "Syntanol DS-10"

Parameter	Value
Appearance at 20 ±5 °C	White to yellowish paste
Melt colour (iodine scale) mg 12/1000 cm ³ , max.	2
Cloud point of 1 % mass fraction of the aqueous solution, °C	64-74
Mass fraction of polyethylene glycols, % max.	4.0
pH of aqueous solution with mass fraction and basic substance 10%	6.0-9.0
Mass fraction of the substance extractable with hexane	8.5
HLB number	13.0

Table 4. Characteristics of reagent "OS-20"

Parameter	Value
Appearance at 20 ±5 °C	Wax-like flakes or solid mass
Melt colour на 12/100 cm ³	6
Appearance of 10% aqueous solution	Transparent colourless liquid without mechanical additives
pH of 10% solution	8.0-10.5
Mass fraction of iron, % max.	0.002
Mass fraction of ash, % max.	0.2
Cloud point of 1% solution of the product in 5% NaCl solution, °C	90-96
HLB number	15.3

Table 5. Characteristics of the reagent "OS-25"

Parameter	Value
Appearance at 20 ±5 °C	White flakes
Cloud point of 1% solution of the product in 5% NaCl solution, °C	76-80
Hydroxide number, mg KOH/g	33-39
pH of 5 % solution	5.0-7.0
Moisture content, %	0.8
HLB number	16.1

The general chemical formula for the proxanols: $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_m(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_n(\text{CH}_2\text{CH}_2\text{O})_m\text{H}$, where for "Proxanol 268" $n=45$, $m=130$, molecular weight 14068, HLB = 16.3

Tests on tar washing were carried out according to the following methodology. Under laboratory conditions, test tar samples and aqueous surfactant solutions were kept in the thermostat at 60°C for 2 hours. Samples at the selected ratio were then stirred with a laboratory paddle stirrer at a rotational speed of 2000 min⁻¹ for 10 min and kept at 60°C for 2 hours. After settling, the water was decanted and the sample taken from the thickness of the washed tar was analysed.

3. Results and discussion

The results of tar quality analysis after washing with aqueous solution of demulsifier "PM" are shown in Table 6.

Table 6. Results of R1-tar washing with aqueous PM demulsifier in 1:1 ratio "tar: solution"

Parameter	Experiment number				
	1	2	3	4	5
Concentration of demulsifier in aqueous solution (dispersion), g/dm ³	0.0	0.25	0.5	0.75	1.0
Characterisation of the washed tar:					
Mass fraction of quinoline insoluble, %	8.15	7.9	7.8	7.7	7.5
Ash content, mass fraction, %	0.200	0.165	0.155	0.150	0.146

The effect of washing the tar with aqueous demulsifier solutions is generally small and does not exceed the data [13-16]. With increasing concentration of demulsifier in aqueous solution,

the quality of tar after aqueous washing improves, with a greater effect of increasing the concentration of the reagent affecting the reduction of quinoline-insoluble substances in washed tar than ash-forming substances. This fact is in favour of the assumption that the content of substances, insoluble in quinoline, decreases at washing with aqueous solutions of demulsifier predominantly due to solubilization.

Increasing the hydrophilicity of the surfactant should promote solubilisation as such surfactants have a HLB number value of between 16–18 units. In addition, it is desirable to increase the concentration of the surfactant solution to increase the efficiency of the process. The results of investigation of tar washing process with the use of aqueous solutions of solubilizing agents are given in Table 7.

Table 7. Results of washing of tar with solutions of various surfactants

Surfactant name	Tar	Surfactant concentration, g/dm ³	Mass fraction of quinoline insoluble, %	Ash content, mass fraction, %
OS-25	R2	1.0	4.2	0.092
		5.0	3.8	0.088
		10.0	3.6	0.087
		15.0	4.1	0.087
	R1	0.0	8.1	0.200
		1.0	6.7	0.150
OS-20	R2	1.0	4.7	0.102
		5.0	4.6	0.086
DS-10	R2	1.0	4.2	0.092
		5.0	4.6	0.102
Proxanol 268	R2	1.0	4.5	0.104
		5.0	4.4	0.090

The results show a higher degree of removal of ash constituents and substances insoluble in quinoline from the tar compared to the previously used demulsifier "PM". The reduction in quinoline insoluble content was reduced by 1.6 to 2.2 % absolute, which is slightly higher for the results [13–16]. For the class of oxyethylated fatty alcohols, increasing the HLB number contributes to a deeper removal of undesirable impurities from the tar. However, "Proxanol 268", with approximately the same number of HLB as that of "OS-25" does not have the same ability to solubilize high-molecular-weight components of the group composition of tar as oxyethylated alcohol "OS-25". The optimum concentration of this reagent in water for a successful washing of tar should be in the range 5–10 g/dm³. An increase in concentration above this limit impairs solubilisation properties of the surfactant solution, probably due to the appearance of new structures.

The effect of ratio "tar: water" phases was investigated by the example of "OS-25" solution with the concentration of 7 g/dm³. The results are given in Table 8.

Table 8. Investigation of influence of "tar : water" phase ratio on efficiency of ash removal process and reduction of quinoline insoluble substances content

Parameter	Value			
Tar R2 for washing, g	100	100	100	100
Solution for washing, g	30	60	100	150
Tar content: water w/w %, g	2.8	3.0	2.7	2.8
Tar content: quinoline insoluble in mass fraction, %	5.3	5.0	3.8	3.7
Tar content: ash mass fraction, %	0.08	0.07	0.09	0.08
Tar solids: ash content: mass fraction, %	0.13	0.11	0.27	0.20

The results show that during washing the "tar: water" phase ratio should be taken as approximately equal in volume with increasing degree of tar removal the ash content of the dry

residue extracted from the aqueous solution increases, which confirms the transition of part of the ash into water soluble state under the action of solubilizers.

An investigation of the effect of temperature on the efficiency of tar washing showed that decreasing the temperature from 50°C has a negative effect on the process. This behaviour may be explained by a sharp decrease in the dynamic viscosity of the tar, which is fixed for most tar at this temperature [29]. Increased viscosity impedes the transport of surfactant through the coal tar thickness.

For a more pyrolyzed tar with a higher content of substances insoluble in quinoline (R3 tar, Table 9) a deeper reduction of substances insoluble in quinoline was obtained by washing with an aqueous surfactant solution.

Table 9. The results of washing of tar with different degrees of pyrolyzation with the solution of the reagent "OS-25" with a concentration of 7.0 g/dm³

Parameter	Tar R3	Tar R4
before washing		
Mass fraction of toluene insoluble, %	14.1	8.4
Mass fraction of quinoline insoluble, %	12.0	5.7
Ash content, mass fraction, %	0.16	0.14
after washing		
Mass fraction of toluene insoluble, %	13.6	6.99
Mass fraction of quinoline insoluble, %	9.2	4.12
Ash content, mass fraction, %	0.138	0.108

Apparently, an increase in the concentration of QI in the tar leads to an increase in the number of particles that can interact with the solubilizer, which leads to a decrease in the content of substances insoluble in quinoline in the washed tar.

At extra-heavy tars with a content of QI above 15–18% the effect of washing with "OS-25" solution decreases, which can be explained by the formation of large aggregates QI [30]. In this case, the specific surface area of the aggregates decreases and the rate of solubilization by surfactant solutions decreases.

Intensification of the tar washing with water and aqueous solutions is possible in the centrifugal field, as closer contact of the phases is ensured. Experimental water washing was carried out under industrial conditions at tar desliming unit in centrifugal field of Flottweg Z4E-4/441 centrifuge at rotational speed 3800–4000 rpm. Ammonia water from the primary gas coolers was pumped into the tricanter feed collector and a homogeneous mixture was fed to the tricanter from the collector circulation line. The composition of ammonia water is given in Table 10, the results of mixture sample analysis before and after the centrifuge are given in Table 11.

Table 10. Composition of ammonia water used to wash the tar, g/dm³

Free NH ₃	Fixed NH ₃	Cl ⁻	CNS ⁻	H ₂ S	Phenol	Pyridine
7.10	0.20	0.21	0.10	2.10	1.48	0.38

Table 11. The results of washing the tar with ammonia water in the centrifugal field of the Flottweg tricanter

Tricanter feed composition	Quality parameters for the tar:			
	before the tricanter		after the tricanter	
	Mass fraction of quinoline insoluble, %	Ash content, mass fraction, %	Mass fraction of quinoline insoluble, %	Ash content, mass fraction, %
Tar (6 % water)	16.8	0.04	15.1	0.03
Water: tar = 50:50	14.5	0.1	11.7	0.04
Water: tar = 30:70	17.1	0.13	15.2	0.04

Experimental industrial tests have shown the possibility of reducing QI in the tar in the centrifugal field by 2.8 % (absolute) due to washing with ammonia water, which contains ammonia–phenolic complexes that have surface–active properties [31].

The mechanism of solubilization by surfactant solutions of highly condensed aromatic structures of substances insoluble in quinoline was examined based on the available data on elemental composition, molecular weight and presence of functional groups [32]. The substances insoluble in quinoline were conventionally represented as a group of associated molecules, the hypothetical composition is shown in Table 12 and Figure 1.

Table 12. Elemental composition of quinoline insoluble substances

Elements	molecule number							Total	Elemental composition		
	1	2	3	4	5	6	7		calculated value	value limits according to [32]	
C	42	42	38	40	40	44	41	287	92.1	92.38	92.83
H	24	24	16	18	18	28	19	147	3.9	2.32	4.14
N				2	2		1	5	1.9	1.95	2.56
S						1		1	0.9	0.25	0.97
O			1			2		3	1.3	1.48	2.04

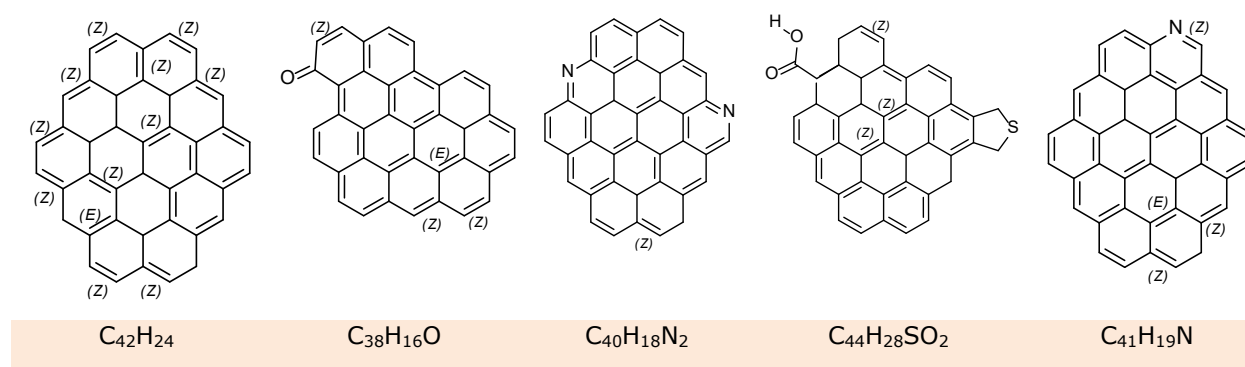


Figure 1. Hypothetical structural formulae of aromatic compounds belonging to the group of associated molecules of substances insoluble in quinoline

According to conventional concepts, substances insoluble in quinoline form aggregates (associates) due to the forces of intermolecular interaction. The elemental composition of the associates indicates a high degree of condensation of the condensed molecule, while IR spectroscopy data provide information about the presence of acid and carbonyl groups and the practical absence of aliphatic hydrogen. Such molecules can form intermolecular bonds with the formation of associates. In the presence of "OS-25" which is fatty alcohol $C_nH_{(2n+1)}O(C_2H_4O)_mH$ with $n=18$ aliphatic carbon and $m=25$ oxyethylated groups establishment of new bonds occurs. Calculation of the intermolecular interaction between the solubilizer ("OS-25") and solubilizer (QI) was carried out using the method of MM2 (Molecular Mechanics 2).

In Chem 3D Ultra, the MM2 method is used to estimate the energy of intermolecular interactions by calculating the total energy of intermolecular interaction (E , kcal/mol). If this energy is higher, it means that the interaction between these molecules is strong and stable. The calculation was performed for two model substances insoluble in quinoline: for an aromatic and a heteroaromatic molecule distinguished by the presence of pyridine-rich nitrogen which attaches a dipole moment to the molecule (0.297 D). To assess the efficiency of solubilization process we calculated energies of intermolecular interaction of two model molecules with aliphatic hydrophobic and polyoxyethylene hydrophilic parts of "OS-25" molecule. The calculated values are presented in Table 13–14.

Table 13. Calculated values of energy of intermolecular interaction (E, kcal/mol), for polar and non-polar model fragment of quinoline insoluble and hydrophilic/hydrophobic part of "OS-25" molecule

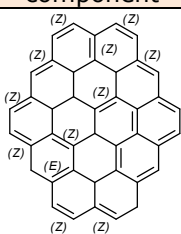
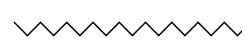
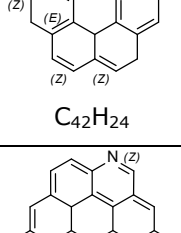
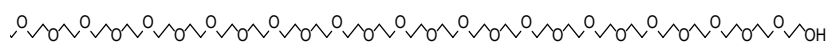
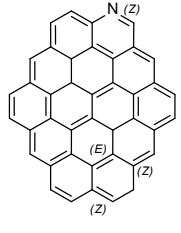
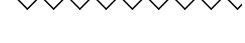
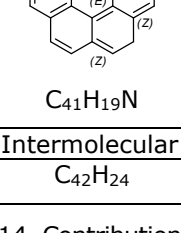
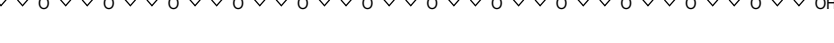
Nº	Solubilisable component	Hydrophobic/hydrophilic part of the "OS-25" solubiliser molecule	E, kcal/mol
1			2655
2			2658
3			329
4			450
Intermolecular interaction between the molecules that are part of QI			
5	C ₄₂ H ₂₄	C ₄₁ H ₁₉ N	2622

Table 14. Contribution of bond type and interactions to total energy, E, kcal/mol, (numbering from Table 13)

Energy components of bond interaction:	Calculation number				
	1	2	3	4	5
tension	523.7	517.7	14.0	23.9	562.0
bending	880.9	839.1	162.7	191.1	747.9
stretch + bend	2.3	9.4	-2.87	1.4	-15.8
rotation	256.2	246.6	75.3	75.1	227.6
van der Waals forces	317.5	384.5	92.5	179.3	291.8
others:	674.6	660.8	-12.7	-20.2	808.3
dipole-dipole interaction			0.2974	-0.4867	
Total energy	2655.2	2658.2	329.19	450.1	2621.9

As follows from the calculations, hydrophobic arenes establish interactions with approximately equal values of intermolecular interaction energy with aliphatic and polyoxyethylene part of the solubilizer. Heteroaromatic substances establish closer bonds with hydrophilic polyoxyethylene chain of "OS-25" molecule.

The above calculation results confirm the position [33] that non-polar hydrophobic organic substances are predominantly solubilized in the hydrophobic core of micelle, and polar hydrophobic substances in polyoxyethylene "shell" of micelle.

The low degree of solubilization of substances insoluble in quinoline is explained by the commensurate value of intermolecular interaction energy between the molecules, included in QI. This prevents effective washing of substances with surfactant solutions and explains the low effectiveness of this method of reducing the content of QI in coal tar.

4. Conclusion

The reduction of substances, insoluble in quinoline, carried out by washing with water, ammonia water, with solutions of surface-active substances, with settling in a centrifugal and gravitational field does not allow reducing their content more than 2–3 % (absolute).

At washing there is a reduction of ash-forming substances of tar, which implies co-sorption of QI on mineral particles of tar. However, an increase in surfactant concentration at washing

the tar with aqueous solutions shows a more effective removal of QI than mineral substances, indicating predominantly their removal due to solubilization by surfactant solutions.

Estimation of energy of intermolecular interaction between hydrophilic and hydrophobic parts of non-ionic surfactant and model components of substances, insoluble in quinoline, showed the reason of low efficiency of solubilization. It lies in the comparability of the value of energy of intermolecular interaction of molecules included in QI with the energy of intermolecular interaction of these substances with the solubilizing agent.

Symbols

QI	quinoline insoluble;
μm	$10^{-6} m$;
cSt	centistokes;
HLB	hydrophile lipophile balance;
MM	Molecular mechanics;
E	total energy, kcal/mol.

References

- [1] Tarasyuk YuYa, Serik DT, Bukka AA, Ivashchenko YeYu, Cheshko FF. Tekhnologicheskiye osobennosti proizvodstva kamennougol'nogo peka iz smesi kamennougol'nykh smol raznykh proizvoditeley i varianty sovershenstvovaniya protsesssa. Uglekhimicheskiy zhurnal, 2012; 5–6: 55–63.
- [2] Rubchevskiy VN, Volokh VM, Zelenskiy VV, Kovalev ET, Kovaleva NI, Bannikov LP. Osobennosti i perspektivy pererabotki khimicheskikh produktov koksovaniya na PAO «ZAPOROZH-KOKS». Uglekhimicheskiy zhurnal, 2014; 1–2: 43–50.
- [3] Hongchao L. CN Patent 202 279 802, 2012.
- [4] Mukina NV, Bannikov LP, Cheshko FF, Achkasova GG. Vliyaniye granulometricheskogo sostava tverdogo dispersnoy fazy kamennougol'noy smoly na effektivnost' yeye vydeleniya v tsentrifuge nepreryvnogo deystviya. Uglekhimicheskiy zhurnal, 2012; 1–2: 34–43.
- [5] Makihiko M. U.S. Patent 4 640 761, 2004.
- [6] Makihiko M. U.S. Patent 4 986 895, 2008.
- [7] Stipanovich J. WO Patent 94/03559, 1994.
- [8] Hima Bindu VNV, Chandaliya VK, Siddiqi H, Dash PS, Ray S, Meikap BC. Role of kinematic viscosity on removal of Quinoline Insolubles from coal tar using wash oil and mixed solvent, Sep. Sci. Technol., 2020; 56(12): 2061–2073.
- [9] Guangxin F. CN Patent 105 670 671, 2018.
- [10] Stadelhofer J. U.S. Patent 4 259 171, 1981.
- [11] An JC, Lee SY, Park JI, Ha M, Shim J, Hong I. Study of Quinoline Insoluble (QI) Removal for Needle Coke-Grade Coal Tar Pitch by Extraction with Fractionalized Aliphatic Solvents and Coke Formation Thereof. Appl. Sci., 2021; 11(7): 2906–2913.
- [12] Yu C, Zhao N, Guo A, Wang Z. Research progress in the removal of quinoline insolubles in coal tar. Chem. Ind. Eng. Prog., 2015; 34(9): 3262–3266.
- [13] Medvedev KP, Khar'kina LM, Zaychenko VM Issledovanie efektyvnosti otstoya kamennougol'noi smoly. Coke and Chemistry, 1970; 9: 29–34.
- [14] Medvedev KP, Privalov VE, Khar'kina LM Issledovanie efektyvnosti novoi skhemy otstoya kamennougol'noi smoly. Coke and Chemistry, 1971; 11: 40–43.
- [15] Mishin IF, Katyukhin VA, Fisich MV. Promyvka smoly v proizvodstvennykh usloviyakh. Coke and Chemistry, 1978; 9: 36–39.
- [16] Amelin AG. Obshchaya khimicheskaya tekhnologiya, Khimiya: Moskva, 1977; p. 400.
- [17] Gnilokvas OP, Mishin IF, Rus'yanova ND, Mochalov VV, Zhdanov VS. Ochistka kamennougol'noy smoly prisadkami. Coke and Chemistry, 1985; 9: 29–32.
- [18] Gnilokvas OP, Chistova GY, Butakova AV, Perovskiy VS, Medvedev GN, Anikin GY, Andreyev LM. Opytno-promyshlennyye ispytaniya ochistki kamennougol'noy smoly prisadkoy AzNII. Coke and Chemistry, 1987; 5: 59–32.
- [19] Rouse JD, Morita T, Furukawa K, Shiao BJ. Solubilization of mixed polycyclic aromatic hydrocarbon systems using an anionic surfactant. Colloids Surf., 2008; 325(3): 180–185.
- [20] Zhu L, Feng S. Synergistic solubilization of polycyclic aromatic hydrocarbons by mixed anionic-nonionic surfactants. Chemosphere, 2003; 53(5): 459–467.

- [21] Pensini E, Harbottle D, Yang F, Tchoukov P, Li Z, Kailey I, Xu Z. Demulsification Mechanism of Asphaltene-Stabilized Water-in-Oil Emulsions by a Polymeric Ethylene Oxide-Propylene Oxide Demulsifier. *Energy Fuels*, 2014; 28(11): 6760–6771.
- [22] He L, Lin F, Li X, Sui H, Xu Z. Interfacial sciences in unconventional petroleum production: from fundamentals to applications. *Chem. Soc. Rev.*, 2015; 44(15): 5446–5494.
- [23] Yu G, Karinshak K, Harwell JH, Grady BP, Woodside A, Ghosh M. Interfacial behavior and water solubility of various asphaltenes at high temperature. *Colloids Surf.*, 2014; 441: 378–388.
- [24] Toledo GFG, Almeida JM, Brito AMM, Batista CCS, Andrade LS, Araujo DR, Icimoto MY. Harvesting of Surfactant-Solubilized Asphaltenes by Magnetic Nanoparticles. *Energy Fuels*, 2022; 36(19): 11839–11848.
- [25] Bai Y, Cheng Y, Hu J, Huang C, Tang S. Research status and Prospect of thermal cleaning technology for oily sludge. *Appl. Chem. Ind.*, 2020; 49(6): 1498–1501.
- [26] Rubchevskiy VM. UA Patent 92 537, 2014.
- [27] Topilnytskyi P, Romanchuk V, Bannikov L, Karchakova V, Chuishchev V, Nyakuma B, Gunka V. Demulsifying compositions for destruction of water coal tar emulsions. *Pet Sci Technol.*, 2022; 12: 1–21.
- [28] Huang HL, Grace Lee WM. Removal of vaporous naphthalene using polyoxyethylenated nonionic surfactants. *J. Air Waste Manag. Assoc.*, 2003; 53(8): 983–991.
- [29] Bannikov LP, Miroshnichenko DV. Adjustment and interpretation of coefficients for coal tar viscosity/temperature equations. *Pet Coal*, 2023; 65(1): 173–182.
- [30] Cheshko FF, Kovalev ET, Martynova AY. Evaluation method of the granulometric composition of quinoline insoluble components of coal tar and pitch. *Pet Coal*, 2019; 61(6): 1337–1342.
- [31] Pasternak AA, Bannikov LP, Skripchenko NP, Butko KA. Opredeleniye poverkhnostnoy aktivnosti ammiachnykh ekstraktov, poluchennykh iz smol gazosbornikovogo i kholodil'nikovogo tsiklov. *Uglekhimicheskiy zhurnal*, 2016; 5: 22–28.
- [32] Privalov VE, Stepanenko MA. Kamennougol'nyi pek. *Proizvodstvo, pererabotka, primeneniye, Metallurgiya: Moskva*, 1981; p. 208.
- [33] Diallo MS, Abriola LM, Weber WJ. Solubilization of Nonaqueous Phase Liquid Hydrocarbons in Micellar Solutions of Dodecyl Alcohol Ethoxylates. *Environ. Sci. Technol.*, 1994; 28(11): 1829–1837.

To whom correspondence should be addressed: Dr. Leonid P. Bannikov, Ukrainian State Coal-Chemistry Institute (SE "UKHIN"), 61023, Kharkiv, 7 Vesnina Str., Ukraine; e-mail: ukhinbannikov@gmail.com