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Evaluation of the Effect of Resin Forming Components on the Quality of Wash Oil for Benzene Recovery from Coke Oven Gas

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Abstract

Quantitative and qualitative assessment of degradation processes of recycled wash oil during operation of benzene units allows to establish the influence of technological factors on oil-specific consumption and to evaluate the quality of fresh oil by additional parameters. It is also desirable to determine the main factors of the processes affecting the yield of resin-like substances and the quality of wash oil. In the article results of monitoring of oils composition, executed by a chromatographic method, in various benzene installations are shown. The prevalence of the formation of indene oligomers over the oxidative polymerization of acenaphthene is stated. Calculation of the thermodynamic properties of the expected products of the polymerization reactions of resin-forming components was carried out using Joback's fragmentation method. The equilibrium composition of oligomerization products was calculated using the Gibbs energy minimization method. Above a certain oil heating temperature (140 °C) the properties of wash oil improve due to a decrease in the melting temperature and molecular weight. This agrees with the available experience of distillation department operation – at wash oil fire heating up to 160-180 °C the specific consumption of wash oil is lower, than at units with insufficient oil heating in steam preheaters.

Keywords: Resin forming components; Wash oil, Oligomer; Thermodynamic parameters.

1. Introduction

Coke-chemical production makes it possible to obtain a wide range of diverse products (including benzene hydrocarbons and naphthalene) from blends of coal [1-6]. For capturing benzene hydrocarbons and naphthalene at coke plants coal tar fraction (wash oil) is widely used, which is a multicomponent azeotropic mixture of aromatic hydrocarbons [7-8], which cannot be separated by conventional distillation. High-melting components contained in the mixture (acenaphthene, dibenzofuran, fluorene, anthracene, carbazole) worsen the quality of the oil [9], so their extraction from wash oil is widely covered in the literature, mainly as a raw material for the production of photoelectric materials. In order to obtain certain components β -methylnaphthalene [10], fluorene [11], isoquinoline [12], nitrogen-containing substances [13], indole [14-15], heterocyclic nitrogen-containing substances [16] etc. are extracted from it. The above variety of methods characterizes wash oil as a very complex physical and chemical system, since many different solvents, alkaline or acid washes and other physical and chemical methods are used to extract the individual component.

The use of wash oil for the absorption of benzene hydrocarbons involves its relatively low saturation (≈ 1.5 -2.5%). When oil is alternately heated and cooled, the absorbing operating properties deteriorate and therefore increased attention is paid both to the quality of fresh oil [17] and to its operating conditions [18-19]. Especially often oil quality is correlated with its corrosiveness [20], formation of deposits on heat and mass transfer surfaces [21], entrainment with

coke gas [22-23], and increased consumption for benzene recovery [24]. As a desirable benchmark, we can give a specific wash oil consumption of 38.07 kg/t of crude benzene, achieved at some enterprises in China [25]. Thus, stabilization of oil quality allows for solving a whole complex of problems in the operation of a benzene plant.

Existing requirements of technical specifications for fresh wash oil cannot reflect all complex operational characteristics, and therefore additional methods of research and an absorbent estimation are actual. For example, the component composition of the oil is defined by a chromatographic method and can bear the information on solidification temperature [26-27], the presence of high-boiling high-melting substances (anthracene), crystallizing substances (acenaphthene) [28], solvents (methylnaphthalenes, quinolines), easily volatile oil components (indene, naphthalene [29]). The content of resin-forming substances that can cause thickening and emulsification of oil (phenols [30], unsaturated compounds) takes a special place. However, at present, there is no consensus on the required content of even phenols and nitrogenous bases in wash oil, more so there are no developments on the desired content of individual oil components, which can serve as markers of polymerization and thickening processes.

In addition to the above-mentioned resin forming agents, crude benzene extracted from oil contains polymerizable unsaturated compounds amylene, hexene, cyclohexene, cyclopentadiene, and cyclohexadiene, while coke oven gas contains ethylene, propylene, butylene, butadiene. It was found that the yield of unsaturated hydrocarbons depends little on the type of coal charge. The yield of ethylene occurs in a wide temperature range, and the combined yield of ethylene and propylene at identical pyrolysis temperatures regardless of the type of coals indicates the insensitivity of the yield of unsaturated hydrocarbons to the type of pyrolyzed coals [31]. Therefore, resin-forming agents are unavoidable and concomitant substances when extracting benzene hydrocarbons from coke oven gas. To increase the stability of wash oil, prevent its losses and increase its cycle of operation it is proposed to carry out hydrotreatment of absorption oil with hydrogen to saturate unsaturated hydrocarbons [32]. Similarly, purification of coke oven gas from thiophene in fine purification for chemical synthesis is proposed [33]. However, such methods are costly and justified in the case of obtaining chemical products with high added value. For traditional installations, it is necessary to search for technological methods to improve the oil stability and to develop criteria for the selection of fresh oil of improved quality.

Particularly sensitive to the economics of the process of capturing benzene hydrocarbons accumulation resin forming components in wash oil. Due to the deterioration of recycled oil, it is necessary to constantly remove and replenish it with fresh wash oil, which is very critical in conditions of decreasing volumes of coal tar processing. At the same time, polymers of the benzene department are a resource for obtaining indene-coumarone resins [34]. Therefore, it is desirable to combine the problem of withdrawal of resin-forming components from recycled oil with obtaining highly concentrated raw materials for obtaining the corresponding resins.

There are alternative views on the causes of wash oil degradation. Spoilage of wash oil is also connected with a propensity to polymerization of such components as acenaphthene, diphenylene oxide and fluorene [35], loss of thermal stability of absorption oil components (acenaphthene, fluorene and phenanthrene) due to their oxidation and polymerization, the interaction of oil components with hydrogen sulfide, ammonia in presence of solids and iron [36-37], the introduction of tar-like components from coke gas [36]. According to [37] such components as hydrogen sulfide and organic sulfur, cyanides, water, ammonia, and tars cause disruption of benzene separation. This leads to the formation of colloids in crude benzene and emulsions in oils. Thus, the formation of benzene polymers is not only a difficult practice but also a scientific problem.

The task of the present study is a quantitative and qualitative assessment of the processes of degradation of recycled wash oil during the operation of benzene compartments due to resin-forming components. It is also desirable to determine the main factors (temperature, concentration) of processes affecting the yield of tar-like substances and the quality of wash oil (viscosity, pour point temperature). In addition, due to the need to obtain valuable components, such as raw materials for the production of photoelectric materials, the mechanism of oil tarring with the participation of resin-forming components could clarify the inevitable

processes of degradation of wash oil when isolating components using expensive solvents (ionic liquids, super-solvents, etc.).

2. Experimental

Changes in the concentration of individual chromatographic components of wash oil during its operation were determined by analysis of daily taken samples of rich and lean oils of benzene units, which were operated during the period of stable operation within the actual regulations of enterprises. To calculate the thermodynamic equilibrium of reactions with the formation of high-molecular compounds the average content of tar-forming components in wash oil was taken in recalculation per 100 kg of oil (Table 1).

Table 1. The averaged concentration of resin-forming components in wash oil

Initial components	Mass, kg/100 kg of oil
indene	1.4
coumarone	0.14
styrene	0.05
thionaphthene	1.4

The concentration of indene in recycled wash oil, according to data from monitoring of benzene plants, fluctuates in the range of 0.4-1.2 %, the content of coumarone is approximately 2-3 times lower, and the content of styrene is almost an order lower [38].

Mass concentrations of wash oil components were determined by the chromatographic method using a chromatograph "Crystal 2000 M" with the software "Chromatec Analytic". The measurement method consisted of direct chromatography of the sample with subsequent calculation of chromatograms and calculation of the mass fraction of benzene hydrocarbons relative to the mass of the "internal standard" added to the wash solution - tetradecane, and higher boiling oil components relative to the mass of the "internal standard" - acetophenone. Conditions of the chromatographic analysis are presented in Table 2.

Table 2. Chromatographic analysis conditions

Parameters	Numerical values
Column thermostat temperature, °C:	
initial	90
final	200
Programming rate of temperature, °C/min	6
Evaporator temperature, °C	200
Detector temperature, °C	250
Volume flow rate of carrier gas, cm ³ /min	30 – 40
Hydrogen flow rate, cm ³ /min	40
Volume flow rate of air, cm ³ /min.	300
Analysis duration, min	55

The directions of transformations of oil polymerization processes were evaluated by constructing the assumed oligomers formed in the interaction of resin forming components presented in Table 1. The properties of supposed products of coal tar wash oil polymerization reactions, namely melting point and thermodynamic parameters (Gibbs energy and enthalpy under standard conditions) were calculated using Joback's fragmentation method. This method calculates the thermophysical properties of the substance on the basis of the group contribution method, taking into account the available basic structural information of chemical substances [39].

The equilibrium composition was calculated by Gibbs free energy minimization. This method is based on the fundamental principle that at the chemical equilibrium of a reaction system the Gibbs energy reaches its minimum of the total energy of the system. The equilibrium constants of the individual reactions are not taken into account, only the expected products of the reactions are designated, and the distribution between them is calculated using mathematical methods to obtain the minimum of the free energy. The summation is performed on

the expected reaction products, which are chosen on the basis of possible combinations of the initial monomers. For each atom that makes up the system, the number of moles remains constant during the process. According to this method, the equilibrium composition is calculated at given temperatures and pressures without taking into account the stoichiometric coefficients while observing the balance of the atoms of the system [40], with the initial concentrations of the reactants corresponding to the average composition of the wash oil. The result of the calculation of the Gibbs energy minimum is a hypothetical equilibrium system, which consists of prearranged components, and the reaction products. To calculate the minimum free energy of the system, the values of the free energy of formation and the enthalpy of formation of the hypothetical reaction products under standard conditions were entered. The calculation was performed as an isothermal process at given temperatures corresponding to the operation of the wash oil in benzene units.

3. Results and discussion

Monitoring of the oil composition by the chromatographic method was performed on two separate units with fire heating of the oil in two different months of steady operation. It is desirable to estimate changes in acenaphthene content, as an indicator of thermal oxidation of aromatic hydrocarbons with their subsequent thickening [41]. Therefore, a comparison of changes in the acenaphthene concentration was performed with changes in the indene content in the rich and lean wash oil. As an index, we took the ratio of indene in the mixture "indene + acenaphthene" by the average monthly concentrations (Table 3).

Table 3 Monthly averages of indene content in "indene+acenaphthene" mixture, % for rich and lean wash oil

Benzene recovery unit:	Wash oil recycled:	
	rich	lean
Nº 1, period 1	3.02	2.81
Nº 1, period 2	3.13	2.86
Nº 2, period 1	4.83	4.60
Nº 2, period 2	4.68	4.50

The results of the study showed the decrease of indene content in its conditional mixture with acenaphthene after distillation of oil when heated to 155-165°C on all units during all periods. At the same time, the indene content in crude benzene did not exceed 1.7 %, and the part of distilled benzene hydrocarbons from circulating oil did not exceed 1.5 %, which indicates a small portion of indene evaporation with crude benzene. The balance of indene and acenaphthene during the distillation of absorption oil is shown in Table 4. The following parameters were taken: average indene content in crude benzene 1.6 %; crude benzene yield from oil 1.5 %; fraction distilled to 180°C in crude benzene – 0.96; acenaphthene content in fraction distilled over 180°C in crude benzene – 19.3 %.

Table 4. Balance of acenaphthene and indene, kg per 1 t of wash oil

Components	Wash oil recycled:		Balance quantity, kg
	rich	lean	
	In wash oil:		
Indene, kg	9.7	9.2	+0.5
Acenaphthene, kg	193	194	-1.0
In crude benzene:			
Indene, kg			0.24
Acenaphthene, kg			0.11
Per estimated indene polymerization, kg			0.26

The data in Table 3 and Table 4 show, that at least the conversions of indene have a priority before the conversions of acenaphthene in the operation of wash oil, and the decrease of indene content during heating should be attributed mainly to its possible polymerization. The

reactivity of indene, according to this evaluation, is higher than acenaphthene, and polymerization processes of unsaturated components prevail over the processes of oxidative polymerization of high-boiling components of the oil.

It is known that indene thermo-polymerization occurs with the formation of a mixture of compounds of different molecular weights, and the average molecular weight of the resulting resin depends on the heating temperature: at 178°C – 886, and at 200°C only 676 [42]. The process proceeds slowly, which is consistent with the industrial practice of wash oil polymer formation. Low oil heating in steam heaters (110-140°C) leads to even greater problems with the clogging of its tube and heat exchanger coils. The higher temperature of oil heating in tube furnaces (160-180°C) allows to maintain low specific consumption of wash oil for benzene hydrocarbons capturing. But proceeding polymerization reactions in the wash oil are complicated by the presence of many parallel proceeding processes, in particular, dilution of indene and coumarone with aromatic hydrocarbons can lead to the interaction of unsaturated hydrocarbons with aromatic ones.

Coumarone polymerization proceeds with a lower degree and at a lower rate than indene. However, this direction of polymerization in the recycled oil takes place, as according to a variety of data, the oxygen content in the pitch residues from the distillation of polymers of the benzene unit increases. This is illustrated by the data in Table 5, which shows the increase in oxygen content during the operation of the circulating oil.

Table 5. Elemental composition of the wash oils and coal tar fractions

Materials	Elemental composition, %				
	C	H	N	S	O
Wash oil [36]	90.21	6.41	1.11	0.27	2.00
Pitch residues of the benzene department [37]	86.40-88.20	5.30	0.99-2.67	2.4-5.25	1.56-3.05
Coal tar [38]	90.9	5.2	2.2	0.5	1.5
Neutral coal tar oils [38]	92.1	5.5	1.1	0.4	0.9
Coal tar high molecular fraction [38]	80.4	5.9	3.3	0.6	9.8
Fresh diesel oil [39]	83.16	1.92	12.67	0.55	1.70
Recycled diesel oil [39]	70.21	1.89	11.63	0.00	16.27
Anthracene oil after treatment with AlCl ₃ at 300°C, [40]	62.3	5.4	0.7	0.5	1.1
Same without catalyst [40]	90.9	5.0	0.9	1.8	1.4
Same under air pressure [40]	90.9-91.8	4.6-4.9	0.9-1.0	0.4-0.5	2.1-2.8

Moreover, the analysis of the group composition of coal tar separates high molecular weight fraction, which is characterized by increased oxygen content, compared with phenols content [43-44]. The above data confirm that the thickening of coal tar and its fractions occur with the participation of oxygen-containing aromatic compounds, and the oxygen content increases as a result of tar forming processes. During the operation of wash oil, the oxygen content also increases, which is explained by the contact of hot oil with air oxygen [45]. The anthracene fraction and wash oil are recovered by coal tar distillation and distilled at 300-360°C and 200-300°C, respectively, containing a number of the same chromatographic components and anthracene fraction can serve to some extent as analogues of wash oil oxidation behavior. However, goal-seeking oxidation of anthracene fraction with air oxygen at 300°C and under pressure during 5-10 h doesn't lead to a significant increase of oxygen content in oil (2.1-2.8 %) and is comparable with the oxygen content in oil obtained by thermal ageing with aluminum chloride or sulfur (1.1-1.4 %) [46]. It is known that aromatic compounds are inhibitors of radical-chain oxidation processes, studies on the oxidation of aromatic hydrocarbons at 100-200°C show that the interaction of air on molten hydrocarbons does not result in oxygen-containing products. In this case, mainly a resin-like mixture of substances with a higher molecular weight than the initial hydrocarbons are formed and the oxidation process quickly stops [47]. Therefore, the data in Table 5 show the validity of transformations of oxygen-containing aromatic components of the oil (including coumarone) with the resulting increase

in the oxygen fraction in the polymers during the operation of the absorption oil even without its oxidation. As in the case of indene, rapid heating of the component mixture leads to the formation of substances with lower molecular weight. Assumptions about the advantage of heating circulating oil in tube furnaces over steam heating with lower and slower heating are in line. It is known that when a substance is heated faster (e.g., pyrolysis), chemical bonds are broken randomly, both weak and strong bonds [48]. Therefore, for example, as a result of high-speed pyrolysis of coal substance, the oxygen content in the semi-coke residue is lower than in slow heating, and the coke yield decreases during fast heating [49]. By the same analogy, in pyrolysis of wash oil substances, slow heating gives a higher polymer yield and the oxygen content in it increases. Rapid heating of oil in tube furnaces reduces the number of resinous products, increases oil stability and reduces its specific consumption [50].

The above data allow considering the expected transformations of wash oil components associated with an increase in molecular weight, along the following lines:

- polymerization to obtain indene, coumarone, and indene-coumarone oligomers;
- styrene polymerization to produce dimers, and copolymers of styrene with indene and thionaphthene.

The selected oil thickening processes can be conventionally referred to as polymerization processes. Similar processes initiated by the oxidation of aromatic hydrocarbons proceed with the release of heat and a corresponding decrease in Gibbs free energy. Free oxygen must be available to create the process conditions, and such processes should be considered separately, out of competition with thickening processes occurring in a predominantly reducing environment. Performed preliminary calculations showed the need to exclude oxidation processes, otherwise, there are no products of polymerization reactions in the equilibrium composition. Moreover, in the practice of operation of benzene compartments reactions with air oxygen are inhibited in the diffusion region due to the low oxygen content in coke oven gas (0.4-1.0% vol.). In addition, oxidation processes in the existing benzene hydrocarbons recovery technology could be suppressed.

Therefore, two isolated systems should be selected for separate consideration: polymerization of indene – coumarone and polymerization of styrene and thionaphthene. For each system, the minimum Gibbs energy at equilibrium reactions composition should be separately determined. Combining above mentioned systems in the calculation of the equilibrium composition by minimizing the Gibbs energy is erroneous since it is impossible to exclude the hypothetical transformations of aromatic structures into each other to obtain products with a more favourable energy state. Previously performed calculations showed that the progression of numerous reactions of styrene with various aromatic compounds (naphthalene, mono- and tri- derivatives, phenanthrene, anthracene) is less likely than polymerization of styrene with the formation of mainly styrene tetramer. The two groups of calculated reaction mixture compositions obtained separately were averaged into a single reaction composition. The estimated compositions of the reaction products and the basic properties of the oligomers formed with the participation of resin forming components are given in Table 6.

The calculation was performed in accordance with the temperature range of absorption and distillation wash oil processes. Maximum low temperatures of wash oil do not go below the temperature of incoming coke oven gas (usually 30-40°C). At units using steam heating, as a rule, oil heating temperature does not exceed 120-140°C, and at fire heating, it is 160-180°C. Table 7 shows the results of the calculation of the equilibrium composition of the reaction mixture formed with the participation of monomers (Table 1).

Indene and coumarone make the greatest contribution to the mass of the formed oligomers due to their higher content in the initial reaction mixture. Styrene reacts completely under the considered conditions, the amount of benzothiophene changes insignificantly, mainly due to the limited resource of styrene.

The determining reactions of oligomer formation are those of the formation of indene and coumarone trimers, especially in the area of low temperatures. The resulting reaction products are a mixture of chains of short length, which corresponds to a degree of polymerization of 2-4. With an

average molecular weight of oligomers of 305-348, indene trimers and indene and coumarone oligomers are the predominant fractions. This degree of polymerization is lower than the traditional indene-coumarone resins obtained from purified raw materials and in the presence of Friedel-Crafts catalysts [38], where the main fraction is a tetramer.

Table 6. Possible compounds of resin forming components and their calculated properties

Oligomers, mole, formed by:				Characteristics of formed components		
styrene	benzo-thio- phene	indene	coumarone	Formula	Molecular weight	Melting point, °C
Indene-coumarone group:						
		1		C ₉ H ₈	116.2	-20.4
			1	C ₈ H ₆ O	118.1	-5.1
		2		C ₁₈ H ₁₆	232.3	150.4
		3		C ₂₇ H ₂₄	348.5	304.5
		4		C ₃₆ H ₃₂	464.6	458.5
		5		C ₄₅ H ₄₀	580.8	612.6
			2	C ₁₆ H ₁₂ O ₂	236.3	181
			3	C ₂₄ H ₁₈ O ₃	354.4	350.4
			4	C ₃₂ H ₂₄ O ₄	472.5	519.7
			5	C ₄₀ H ₃₀ O ₅	590.7	689.1
			6	C ₄₈ H ₃₆ O ₆	708.8	858.5
		1	1	C ₁₇ H ₁₄ O	234.1	165.7
		1	2	C ₂₅ H ₂₀ O ₂	352.4	335.1
		2	1	C ₂₆ H ₂₂ O	350.5	319.8
		2	2	C ₃₄ H ₂₈ O ₂	468.6	489.1
		3	1	C ₃₅ H ₃₀ O	466.6	473.8
		1	3	C ₃₃ H ₂₆ O ₃	470.6	504.4
		1	4	C ₄₁ H ₃₂ O ₄	588.7	673.8
		2	3	C ₄₂ H ₃₄ O ₃	586.7	658.5
		3	2	C ₄₃ H ₃₆ O ₂	584.7	643.2
		4	1	C ₄₄ H ₃₈ O	582.8	627.9
		1	5	C ₄₉ H ₃₈ O ₅	706.8	843.2
		2	4	C ₅₀ H ₄₀ O ₄	704.3	827.9
		3	3	C ₅₁ H ₄₂ O ₃	702.9	812.6
		4	2	C ₅₂ H ₄₄ O ₂	700.9	797.3
Styrene-benzothiophene group:						
1				C ₈ H ₈	104.1	-68.9
	1			C ₈ H ₆ S	134.2	51.8
	1	1		C ₁₇ H ₁₄ S	250.4	222.6
4				C ₃₂ H ₃₂	416.6	204.6
1				C ₁₆ H ₁₄ S	238.3	165.9

The formation of oligomers when heating the absorption oil is a temperature-dependent process. As the temperature of heating oil before the distillation column rises, the total mass yield of oligomers increases. For indene and coumarone, the yield of all possible trimer combinations decreases with increasing temperature, while the yield of dimers and tetramers increases slightly. No higher-order oligomers are formed. The yield of dimers in the reaction of indene with thionaphthene increases with increasing temperature, especially in the oil heating region of 120-180°C. The yield of dimers in the reaction of thionaphthene with styrene, on the contrary, increases when heated to 100°C, and the formation of styrene tetramers is reduced in favour of the formation of reaction products with thionaphthene. Of all the resin forming components for the considered reactions styrene is consumed completely, also there is a very high thermodynamic probability of using up indene and coumarone (about 91-98% of each substance).

Table 7. Equilibrium concentrations of resin forming components and their oligomers in wash oil resulting from polymerization reactions

Mole of compounds formed by				Temperature, °C									
indene	coumarone	styrene	benzo-thiophene	30	50	60	70	80	100	120	140	150	180
		1		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	1			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.03
			1	1.39	1.37	1.36	1.35	1.34	1.31	1.28	1.23	1.20	1.06
1				0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.03	0.09
2				0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.02	0.05
3				1.19	1.19	1.18	1.17	1.17	1.14	1.09	1.03	0.98	0.79
4				0.01	0.02	0.02	0.02	0.03	0.04	0.06	0.07	0.08	0.09
	2			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	3			0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
	4			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1	1			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
1	2			0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.05	0.05	0.04
2	1			0.27	0.27	0.27	0.26	0.26	0.26	0.25	0.24	0.23	0.19
2	2			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.002
1	3			0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.0003
1			1	0.00	0.01	0.01	0.01	0.02	0.05	0.10	0.19	0.25	0.51
		4		0.04	0.03	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.00
		1	1	0.02	0.05	0.06	0.08	0.09	0.11	0.11	0.11	0.11	0.11
Mass of oligomers, kg100 kg of wash oil				1.60	1.62	1.63	1.64	1.65	1.67	1.70	1.73	1.75	1.81
Mass of monomers, kg100 kg of wash oil				1.39	1.37	1.36	1.35	1.34	1.32	1.29	1.26	1.24	1.18

Table 8. Contribution of entropy and enthalpy to the change of Gibbs energy of the main polymerization reactions

Reactions with obtaining	Values of thermodynamic parameters of reactions at standard conditions		Values of free Gibbs energy of reactions at temperature, °C					
	S, KJ/(mol×K)	ΔH, KJ/mol	30	60	90	120	150	180
diindene	-0.17	-46.3	4.4	9.5	14.5	19.5	24.5	29.6
triindene	-0.37	-101.4	11.0	22.1	33.2	44.3	55.5	66.6
tetraindene	-0.57	-156.6	17.5	34.7	51.9	69.2	86.4	103.6
pentaindene	-0.78	-211.7	24.0	47.3	70.7	94.0	117.3	140.7
indene+coumarone	-0.167	-46.2	4.3	9.3	14.3	19.3	24.3	29.4
indene+dicoumarone	-0.37	-101.3	10.9	22.0	33.1	44.2	55.3	66.4
diindene+coumarone	-0.37	-101.4	10.9	22.0	33.1	44.2	55.3	66.4
diindene+dicoumarone	-1.0	-157.0	17.4	34.6	51.8	69.0	86.2	103.4
indene+thionaphthene	-0.2	-46.3	4.4	9.5	14.5	19.5	24.5	29.6
styrene+thionaphthene	-0.167	-98.90	-48.2	-43.1	-38.1	-33.1	-28.1	-23.0
tristyrene	-0.33	-192.70	-93.3	-83.4	-73.6	-63.7	-53.9	-44.0
tetrastylene	-0.43	-271.90	-140.6	-127.6	-114.6	-101.6	-88.6	-75.7

It is known that polymerization processes are always entropically unprofitable, but for the reaction to proceed it is necessary that changes in entropy are not as significant as changes in enthalpy. Thus, the entropic factor, which hinders the polymerization reaction, begins to show itself as the temperature rises. Values of thermodynamic constants of the main reactions under consideration are presented in Table 8.

As the number of links in the indene derivative chain increases, the entropic contribution to the ΔG of the reaction decreases the thermodynamic probability of the process, while the enthalpic contribution, on the contrary, increases it. However, as the reaction product chain grows, the enthalpic contribution is insufficient. As the temperature increases, the entropic factor increases the ΔG of the polymerization reaction of indene and its derivatives. But since dimers are more likely to form than trimers, indene monomers appear in the equilibrium reaction mixture as the equilibrium shifts toward the formation of starting substances as the temperature increases.

For styrene, the enthalpic factor prevails over the entropic factor as the chain grows, so the probability of tetramer formation is much higher than the probability of dimer and trimer formation. For the reaction of styrene with thionaphthene, $\Delta G < 0$, but this reaction competes with styrene polymerization reactions. At the existing concentration of styrene in the initial mixture, the degree of conversion of thionaphthene is relatively low (24%).

The calculated potential amount of oligomers formed when heating the oil from 120 to 180°C is 1.7-1.81 kg/100 kg of wash oil. This mass is comparable to the amount of distilled benzene from the absorption oil, i.e. in conversion, it can reach ≈ 1000 kg/t of crude benzene. The practice of work of benzene units with high specific consumption of coal tar wash oil shows that this value can reach 400-450 kg/t. Consequently, the polymerization potential of oil is not fully realized in practice. In the analyzed temperature interval of oil heating, the thermodynamic probability of formation of oligomers with a molecular mass of 305-333 is significantly higher than the molecular mass of high-boiling components of wash oil (anthracene 178; phenanthrene 178; fluorene 166).

For the obtained equilibrium composition of the wash oil, it is of interest to the change in the operating characteristics of the absorbent. The degree of thickening is displayed by an increase in the average molecular weight, which is accompanied by a deterioration in viscosity properties and an increase in the pour point temperature.

The reaction mixture (mixture of resin forming components and polymerization reaction products) is a heavily weighted part of wash oil relative to other conditionally inert components. The molecular weight of the weighted part at various process temperatures was calculated using the formula:

$$MW = \frac{\sum_{i=1}^{i=n} (MW_i \times G_i)}{\sum_{i=1}^{i=n} G_i} \quad (1),$$

where: i – the component number; n – the number of components; G_i – the mass of the component in the equilibrium composition, kg; MW_i – the molecular mass of the component in the reaction mixture.

The average melting temperature of the mixture components was calculated using the formula:

$$t_{\text{melt}} = \frac{\sum_{i=1}^{i=n} (t_i \times G_i)}{\sum_{i=1}^{i=n} G_i} \quad (2),$$

where: t_i – melting temperature of the component in the reaction mixture

The increase in the viscosity of the polymer solution in the solvent (or the heavy weighted part of wash oil) correlates with the increase in the molecular weight (MW) in accordance with the Mark-Houwink equation [51]:

$$\eta = K \times (MW)^\alpha \quad (3),$$

where: K and α are substance constants; η – reduced viscosity.

The increase in the pour point temperature is associated with the formation of substances with a high melting point. According to the data in Tables 1,6,7 the basic properties of the reaction mixture depending on the formation temperature were calculated (Figure 1).

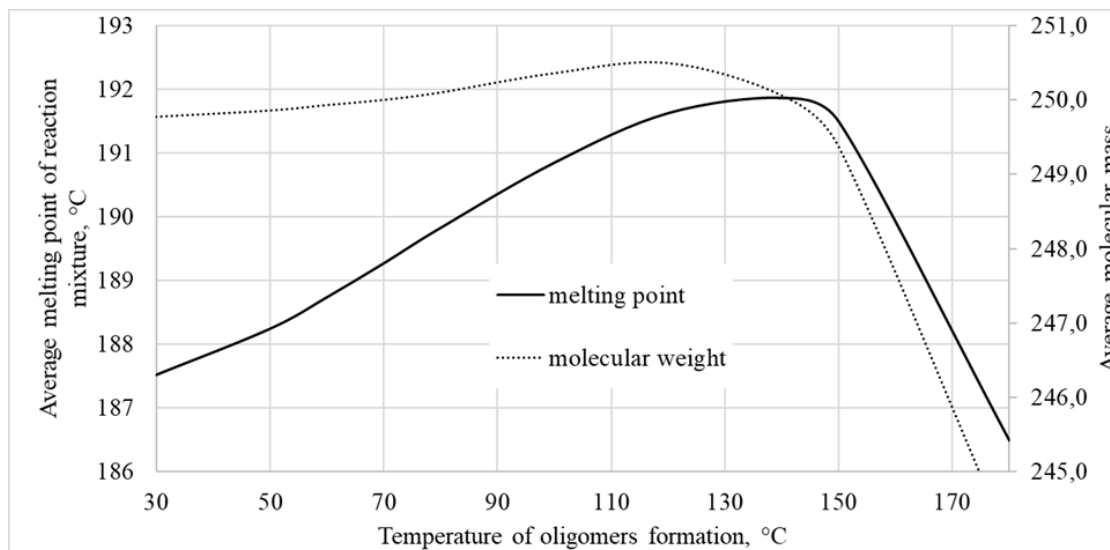


Figure. 1 Average values of melting temperature and molecular weight for the equilibrium reaction mixture

It follows from the above data that the dependence of the molecular weight and melting temperature of the reaction mixture of wash oil formed from resin forming components on the heating temperature has an extreme character. Above a certain oil heating temperature (140°C) the properties of wash oil improve due to a decrease in the melting temperature and molecular weight. This agrees with the available operating experience of benzene units: – when temperature of oil fire heating up to 160-180°C specific consumption of absorbing oil is lower, than at installations with insufficient oil heating. Especially high values of specific consumption have plants, where oil heating is carried out by heating steam with low energy parameters and with a prolonged residence time in the steam preheater. Therefore, in order to reduce the molecular weight of oligomerization products of resin forming components (correspondingly viscosity), as well as to reduce the formation of substances with a high melting point (the pour point temperature) wash oil should be heated to sufficiently high temperature

(150-180°C). This will eventually lead to improvement of the absorbing properties and to reduction of oil consumption associated with the transformation of resin forming components.

4. Conclusion

Monitoring of the oil component composition showed the prevalence of indene polymerization processes over the thermochemical oxidative polymerization of acenaphthene as an indicator of oil thickening under the influence of oxygen. Therefore, indene content can serve as a marker of the resin forming components content and oil quality in general. Establishing the mechanism of oligomer formation from wash oil resin forming components makes it possible to influence the oil specific consumption in the existing technology. Previously, it was believed that the initiation of polymerization by flame heating allows to convert potential resins into actual resins, blew them down as polymers and further exploit the oil as free of potential resins. However, performed thermodynamic calculations have shown that the potential resins can be formed in amounts up to 1000 kg/t of crude benzene, which is about twice the maximum known in practice. But the advantages of flame heating are as follows: when the oil is heated above 140 °C the molecular weight and melting point of oligomers decreases, which leads to lower viscosity and precipitation temperature. This to some extent improves the operating properties of the circulating wash oil compared to lower heating before distillation.

Symbols

S – entropy; *H* – heat of formation; ΔG – Gibbs energy; *MW* – the molecular mass of the component; η – reduced viscosity.

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