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VISCOSITY EVALUATION OF THE MIXTURE OF COAL TARS FROM COLLECTION MAIN AND PRIMARY COOLER ON THE BASE OF RHEOMETER MEASUREMENTS AND EMPIRICAL FORMULAS

Наведено результати експериментального визначення в'язкості смол газозбірникового і холодильникових циклів при їх змішуванні. Було виміряно значення динамічної в'язкості газозбірникової і холодильникової смоли при змішуванні в інтервалі температур 55–80 °C. Температурна залежність більш виражена для більш в'язких сумішевих композиций. Встановлено аномальне зниження в'язкості від прогнозованих значень за емпіричними залежностями при додаванні 5–20 % мас. холодильникової смоли до газозбірникової

Ключові слова: в'язкість суміші, емпіричні залежності, смола газозбірникового та холодильникового циклів

Приведены результаты экспериментального определения вязкости смол газосборникового и холодильникового циклов при их смешивании. Измерены значения динамической вязкости газосборниковой и холодильниковой смол при смешении в интервале температур 55–80 °C. Температурная зависимость более выражена для более вязких смесевых композиций. Установлено аномальное снижение вязкости от прогнозируемых значений по эмпирическим зависимостям при добавлении 5–20 % масс. холодильниковой смолы к газосборниковой

Ключевые слова: вязкость смеси, эмпирические зависимости, смола газосборникового и холодильникового циклов

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1. Introduction

Coal tar is the second largest product of coking plant after coke. The tar is unique and irreplaceable raw source of condensed aromatic compounds, oils and pitch [1]. Recovery of tar from the high temperature coking process takes place during the cooling and partial condensation of the volatile products from coke oven. Condensation occurs twice while cooling gas processes: in the collecting main (≈75–90 °C) and in the primary gas cooler (PGC) to ≈25–40 °C.

As the result of two step condensation a heavy tar called «from collecting main» and a light tar called «from primary cooler» are produced in the condensation section of the chemical coking plant shop. Thus, in practice, all coal

tar produced is a mixture from two cycles. Coking process parameters, the quality of the coal charge, its humidity, the gas temperature cooling regime result in the certain ratio and properties of condensed tars. Mixing of tars is widely used for reducing the heavy tar viscosity thus the decanting process is enhanced with the aim to separate the solid matters and water from tar. The mixing of tars is also used for spraying of the inner PGC gas space because the tar from collecting main has a high potential ability for absorption of naphthalene [2–5].

PGC spraying with coal tar and coal tar emulsion is a highly efficient process technique to dissolve the sublimated naphthalene from the coke oven gas. Only tar content in emulsion is now regulated in the process of PGC washing. At the same time heavy tar content increasing results in higher viscosity of tar mixture and the prevalence of light tar content reduces the solubility of naphthalene in the mixture. It is very important to control the viscosity of the final tar mixture, as well as the content of naphthalene while blending. Coal tar contains solid, liquid or gaseous particles dispersed in a multi-component mixture of organic compounds that is a dispersion medium. Tar mixture viscosity is not an additive value [1, 6, 7].

Besides PGC washing, mixing process is used for lowering the viscosity of tar to improve the sedimentation of the entrained coke chamber coal and coke particles. Viscosity is a measure of some tar grades in accordance with applicable specifications.

In addition the values of viscosity of the tar and its mixtures must be taken into account when performing engineering design, process optimization, evaluation of the dimensionless parameters (Reynolds, Prandtl), mixing energy calculation, computing the parameters of pipelines, etc.

2. Literature review and problem statement

In recent times, the rheological properties of coal tar are determined mainly as individual samples in the case with soil remediation from water-insoluble organic contaminants [8]. In this situation, the tar mixture viscosities are evaluated from the different processes of unknown origin. Moreover, the test samples were exposed to the process of so-called tar aging. This point brings some distortion in tar quality and the viscosity values are in a fairly wide range of 20–100 cP. [9] Thus, the processes of tar oxidation and filtration through the soil lead to an overestimation of density; in addition, such samples cannot be identified by their origin to certain technological processes.

The viscosity dependence of coal tars and pitches on temperature was estimated in [10]. Logarithmic correlation was established, but it had been obtained for substances with a viscosity higher than 104 cP. This range of viscosity values does not match with our investigation interval of tars rheology from collecting main and from primary cooler.

Temperature dependence of coal tar was investigated in order to optimize the process of tar heating before fractionation. In this temperature range the viscosity of the coal tar is significantly reduced and approaches the nature of the flow of Newtonian fluids. These figures were obtained in the temperature range of 100–420 °C [11]. At such temperatures, the rheological properties of the tar significantly differ from its behavior during tar recovery and processing in coking plant condensation section of chemical shop.

Lowering the viscosity of coal tar pitch as the temperature increases is very sensitive and the value is even lower than the viscosity of ethylene resins. The idea is therefore proposed to use coal tar to replace the water quenching in the gasification process. The rheological properties of coal tar were investigated from the point of view of the components content in the temperature range of the corresponding stage of gasification processes (200–250 °C) [12]. It is noted that an increased content of aromatic olefins had resulted in viscosity increasing with aging. The changes of the tar rheological properties are not of importance due to such aromatic olefins content in the tar recovery process in condensation section.

Often the rheological properties of coal tar mixtures must be adjusted for their use in various applications. In [13] rheometric measurements were carried out when mixing with special additives in order to reduce the viscosity. These investigations cannot be extended to prediction of the viscosity of the coal tar mixture, since such additives are foreign to the coal tar nature.

The coal tars from isolated cycles of collecting main and primary coolers are not recovered in almost all coking plants of Ukraine. This leads to an advantageous development of rheological investigation of resulting tar mixtures, rather than individual tar from isolated cycles. Product technical specifications express the tar viscosity in special units that cannot be converted into the absolute values of the dynamic or kinematic viscosity.

On Ukrainian coking plants the viscosity of coal tars and mixtures thereof is measured on viscometers using uncommon units, which cannot be transformed into the system ones. Besides, light and heavy tars individually are investigated insufficiently. Coal tar as the commercial product is formed from a mixture of tars and processed in large enterprises in the electrode pitch. The current situation of reducing the production capacity has increased the tar requirements for the domestic tar. The main reason is a limited possibility of blending with tars from other producers. The tar viscosity is an integral characteristic since it reflects the structures of flow units and the molecular weight itself. The accuracy and reliability of viscosity measurements are enhanced by the spread of modern rheometers.

At the same time, there are methods of predicting viscosity which are used to evaluate petrochemical products. It is known that the viscosity value is not additive, mixed petroleum products viscosity is always less than one calculated by the additivity rule [14]. The higher the viscosity value of the blend components, the higher the error of additive determination of the estimated value.

Thus, it is necessary to complement existing researches by the rheology of coal tars that are produced on mainly imported raw materials base. This is essential for the process control of the whole complex of the primary cooling processes of the modern coking plant. It is also required to assess the applicability of the formulas for calculating the viscosity of petroleum products to predict the viscosity of a mixture of coal tars.

3. The purpose and objectives of the study

The aim of this work was to obtain the rheological properties of coal tar by mixing two different samples from one chemical plant: the most viscous heavy tar and the lightest one. To achieve the goal the following tasks were formulated:

— to compare the main characteristics of the samples of both cycles as for pitch and oils production requirement. This is especially important according to lowering Ukrainian coking coal in coal charge;

— to get the value of the dynamic viscosity of the individual tar samples by viscometer of the rotary type in the range of the storage temperature (55–80 °C) and processing in the condition of the condensation section. Evaluate the viscosity of tar mixtures, especially in the range of small light tar additives;

— to investigate the applicability of the existing predictive equations for estimating the viscosity of the petroleum oils mixture to a mixture of coal tars;

— to identify the physical sense of the coefficients of the prediction equation, taking into account the existing ideas about the nature of coal tar.

4. Characteristics of the tar samples, methods for measuring and predicting the viscosity of mixtures

Samples of coal tar were selected from gas collecting main and primary coolers cycles. Analyses of the coal tar specification are presented in Table 1, 2.

Table 1

Indicators of coal tar quality

Tar samples from	Density, 25 °C, g/sm³	Water content, %	Insoluble matter		Ash content, dry water free basis, %
			in toluene (TI)	in quinoline (QI)	
primary cooler	1188	3.0	9.2	6.8	0.09
gas collecting main	1207	4.1	15.3	8.0	0.11

Table 2

Compound content, % w., and boiling range of tar samples

Compound	Tar samples from	
	primary cooler	gas collecting main
Benzene	1.03	0.21
Total aromatic, low boiling	4.81	1.01
Indene	5.64	1.22
Naphthalene	23.03	10.70
Benzothiophene	0.65	0.40
β-methylnaphthalene	2.47	1.21
α-methylnaphthalene	2.60	1.51
Dimethylnaphthalenes, total	1.26	1.20
Acenaphthylene	0.04	0.43
Acenaphthene	1.87	1.80
Dibenzofuran	0.67	1.84
Fluorene	1.15	1.45
Non identified compounds	0.34	1.13
Antracene + phenantrene	2.3	5.08
Heavy non identified compounds	1.53	8.31
Boiling range, °C, % w.		
to 210	578	4.11
210–235	16.14	13.12
235–300	11.60	8.73
300–360	8.85	13.30
Pitch	57.63	60.74

Mixing of tar samples was carried out by preheating at 70 °C followed by stirring at laboratory homogenizer with minimum rotational speed and then thermostated. Coal tar from the primary cooler was added to the gas collecting main tar from 5 to 60 %, as in industrial processes. The test range has been wider than it was possible in a coking plant (up to 40 % light tar content).

The tar viscosity was measured in the temperature range of 55–80 °C by rotary viscometer Brookfield DV2T with thermosel at a shear rate of 186 sec^{-1}. The resulting viscosity values were averaged from five parallel measurements. The temperature range for measurements corresponded to tar processing and storage conditions in coking plant condensation section.

The most common empirical equations [14] were used for the predictive evaluation of viscosity of the mixture of coal tar as it had been used normally for petrol oil blends. Polynomials with more than two coefficients were not taken into account while reviewing the equations available in the literature sources. Although these equations more accurately fitted, to interpret the physical meaning of coefficients of such equations was practically impossible.

The correlation coefficients (function «CORREL» in Excel format) were used to determine the relationship between empirical and obtained data groups.

In addition the average relative deviation of the calculated values from experimental data was calculated by varying the coefficients a, b, c in the Vogel equation for the minimal value δ:

$$\delta = \frac{1}{n} \sum_n \left| \frac{\eta_e - \eta_t}{\eta_e} \right|, \tag{1}$$

where η_e — the experimentally obtained value of viscosity, cP; η_t — the estimated value of viscosity, cP; n — number of experimental values.

The correlation coefficient reflects the «type» of functional dependence, and the convergence of the results determined by the mean of relative deviation. Therefore, a double assessment of suitability of the calculated and experimental data was made. New models of temperature dependencies of viscosity at various additives can be considered adequate for the values of correlation coefficients above 0.95 and average relative deviation of not greater than 0.05, which is acceptable for engineering calculations of chemical and technological processes in the majority of cases.

5. The results of the viscosity measurements of tars and their mixtures

Figures of dynamic viscosity of samples were measured and then transformed to kinematic viscosity using density values. The densities of the tar mixtures were calculated on the basis of the additivity principle. The kinematic viscosity values are shown in Table 3.

The obtained values of viscosity of tar from gas collecting main correspond approximately to the range of 19–95 cP. This interval is typical for a coal tar with a density of 1.160–1.170 g/cm³ [13]. With an increase in the proportion of light tar the viscosity of mixture decreases, indicating about the lower molecular weight of tar from a primary color. This is confirmed by the temperature range of tar condensation, as it was mentioned above.

Table 3

Kinematic viscosity (cSt) of the tar from gas collecting main when adding light tar

Tempera-ture, °C	Tar from primary cooler content, % w.						
	0.0	5.0	10.0	20.0	40.0	60.0	100.0
55	87.0	75.5	60.6	54.0	50.9	36.8	24.4
60	75.4	64.7	53.1	45.7	43.8	31.8	20.2
65	59.7	51.4	44.0	38.6	34.2	25.9	18.5
70	46.4	42.3	36.1	30.8	28.3	21.7	16.2
75	36.5	34.0	30.3	25.8	23.3	19.2	14.3
80	29.0	28.2	24.1	20.8	19.6	17.6	13.9

If calculate the viscosity of the mixture according to the additivity rule, any measured values of the mixture are less than calculated figures. This fact is established to the viscosity of oil mixture [14].

6. Evaluation of viscosity temperature dependences of mixtures by predictive equations

The measured viscosity values exponentially decreases with increasing temperature. For heavy tars with higher initial viscosities, higher temperatures give a greater reduction in viscosity (58 cSt) than light tars from a primary cooler (11 cSt). The results show that the temperature effect is more important for viscous tars.

The most rapid decrease in viscosity with temperature growth occurs in lower temperature ranges. It follows that a significant improvement in viscometric properties can be achieved by tar heating at a relatively low temperature range.

Measurement results approve the statement that the viscosity of the mixture is not an additive value, and viscosity of the mixture of tars from gas collecting main and primary cooler showed significant deviations from linearity.

Various predictive formulas were used to evaluate the viscosity of liquid mixture. Currently the most well-known methods of viscosity blend predicting are the Refutas equation and the Kendall-Monroe one [14].

The Refutas equation is based on the calculation of the viscosity index of blended components (by ASTM D 7152), and the indices are subject to the additivity rule. The resulting index of the blend is converted into the viscosity of the mixture:

$$A_i = 14{,}534\ln\left[\ln(\mu_i + 0{,}8)\right] + 10{,}975 \ (i = 1, 2\ldots), \tag{2}$$

$$A_{1,2} = x_1 \times A_1 + x_2 \times A_2, \tag{3}$$

where x_i — mass fraction of the component i; A_i — viscosity index of the component i; $A_{1,2}$ — viscosity index of the mixture; μ_i — kinematic viscosity of the component i.

The viscosity of the mixture is calculated by the formula (4):

$$\mu_{1,2} = \exp\left(\exp\left(\frac{A_{1,2} - 10{,}975}{14{,}534}\right)\right) - 0{,}8. \tag{4}$$

In our case light tar from the primary cooler and heavy one from the gas collecting main were taken as the compo-

nents of the mixtures. Table 4 shows the results of calculation of viscosity indices and predicted values of tar mixtures.

Table 4

Prognostic values of the viscosity mixture by the Refutas equation

x light tar	0.0	0.05	0.10	0.20	0.40	0.60	1.0
x heavy tar	1.0	0.95	0.90	0.80	0.60	0.40	0.0
t, °C	Viscosity indices values						
55	32.8	32.5	32.3	31.8	30.9	29.9	28.0
60	32.3	32.0	31.8	31.3	30.2	29.2	27.2
65	31.5	31.3	31.0	30.5	29.6	28.6	26.8
70	30.6	30.4	30.1	29.7	28.8	27.9	26.1
75	29.7	29.5	29.2	28.8	28.0	27.2	25.5
80	28.7	28.6	28.4	28.1	27.4	26.7	25.3
	Predicted values of tar mixtures						
55	87.0	80.8	75.2	65.3	49.9	38.8	24.4
60	75.4	69.8	64.8	55.9	42.3	32.5	20.2
65	59.7	55.8	52.2	45.9	35.8	28.4	18.5
70	46.4	43.7	41.2	36.7	29.4	23.9	16.2
75	36.5	34.6	32.8	29.6	24.4	20.2	14.3
80	29.0	27.8	26.8	24.7	21.2	18.3	13.9

The viscosity of the mixture can be figured on the basis of the calculation of the average viscosity of the cube root of the components by the Kendall-Monroe equation:

$$\mu_{1,2}^{1/3} = x_1\mu_1^{1/3} + x_2\mu_2^{1/3}. \tag{5}$$

Table 5 states the calculated values of the tar mixtures viscosity by the equation (5).

Table 5

Prognostic values of the viscosity of the tar mixtures on the basis of the Kendall-Monroe equation

Tempera-ture, °C	Tar from primary cooler content, % w.						
	0.0	5.0	10.0	20.0	40.0	60.0	100.0
55	87.0	82.6	78.3	70.2	55.7	43.4	24.4
60	75.4	71.4	67.6	60.4	47.6	36.7	20.2
65	59.7	56.8	54.1	48.8	39.4	31.3	18.5
70	46.4	44.4	42.4	38.7	31.8	25.9	16.2
75	36.5	35.0	33.6	30.9	25.9	21.6	14.3
80	29.0	28.1	27.1	25.4	22.1	19.1	13.9

The above equations are empirical dependencies, and do not contain a physical sense and have no theoretical interpretation. There are no data on their practical applicability and accuracy of predicting for the viscosity of coal-tar mixtures by the equation (2)–(5).

The viscosity of a mixture of ideal liquids can be calculated from the Arrhenius equation:

$$\ln\eta_{1,2} = x_1\ln\eta_1 + x_2\ln\eta_2, \tag{6}$$

where x_1, x_2 — the mole fractions of components in the liquid mixture.

To calculate the mole fraction of tars it is necessary to determine appropriate values of molecular weights. It is known that the average molecular weight of coal tar is a purely notional concept since the coal tar has several thousands of individual compounds, most of which are not identified. The values of molecular weight fractions instead of coal tar are often used because of the special rheological properties of coal tar and its low solubility in water. However, in the source [13] it is indicated that the average molecular weight of a sample of coal tar is equal to 215 atomic mass units.

The partial pressure of tar vapor of coke oven gas in the primary cooler and in the gas collecting main may be taken into account to calculate the molecular weight.

The correlation between these values was obtained on the basis of the Clapeyron-Clausius equation as a function of temperature in [15]:

$$P = \alpha \times \exp\left(\frac{-\beta \times M^{\gamma}}{T}\right), \tag{7}$$

where P — partial pressure of resin vapors, atm; M — average molecular weight of the tar; T — temperature, K; α, β, γ — coefficients of the equation.

The α, β and γ coefficients were chosen according to [14]: α = 87060; β = 299; γ = 0.59.

Calculations were made for tar content in gas collecting main (5 g/m³ at 80 °C) and in gas primary cooler (0.5 g/m³) at 35 °C. Average molecular weights of heavy and light tars were established, respectively, 196 and 190, by using the Fletcher equation. Table 6 shows the calculated values of the viscosity of the tar mixtures according to the equation (6).

Table 6

Prognostic value of the viscosity of the tar mixture on the basis of the Arrhenius equation

Tempera-ture, °C	Tar from primary cooler content, % w.						
	0.0	5.0	10.0	20.0	40.0	60.0	100.0
55	87.0	81.5	76.3	67.0	51.8	40.2	25.1
60	75.4	70.4	65.8	57.6	44.1	33.9	20.8
65	59.7	56.2	52.9	46.9	37.0	29.3	19.0
70	46.4	44.0	41.7	37.4	30.3	24.5	16.7
75	36.5	34.7	33.1	30.1	24.9	20.7	14.7
80	29.0	27.9	26.9	24.9	21.5	18.5	14.3

Assessment of the calculated and experimental data is shown in Table 7.

Table 7

The correlation coefficients (K) and average relative deviations (δ)

Tempera-ture, °C	Equations					
	Refutas		Kendall Monroe		Arrhenius	
	K	Δ	K	δ	K	δ
55	0.965	0.072	0.952	0.112	0.962	0.083
60	0.967	0.071	0.954	0.110	0.963	0.079
65	0.977	0.075	0.962	0.113	0.973	0.089
70	0.977	0.064	0.962	0.095	0.973	0.075
75	0.985	0.045	0.973	0.072	0.981	0.055
80	0.958	0.056	0.945	0.070	0.954	0.060
Average	0.972	0.064	0.958	0.095	0.968	0.073

Thus, the most applicable empirical model for viscosity evaluation of tar mixture is the Refutas equation. Deviations of the predictive values from measured for the mixture of liquids, calculated by the Arrhenius equation, are due to the presence of the interaction energy between different molecules when mixed.

Fig. 1 shows the curve types for calculated and measured viscosities with the greatest deviation from the ideality (for 55 °C).
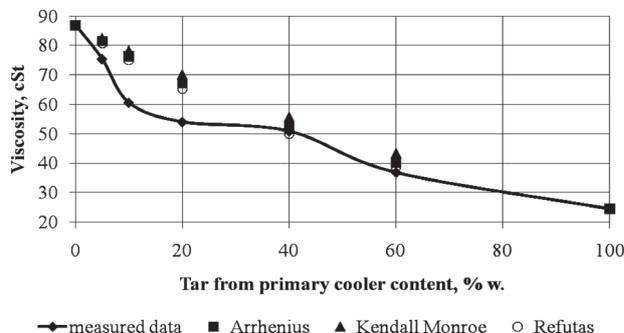
Fig. 1. Comparison of the calculated and experimental data of viscosity at 55 °C

As it follows from Fig. 1 there are significant deviations of viscosity from linearity and from calculations when 5–20 % of light tar adding. This S-shaped type of viscosity curve is typical for systems with highly polar compounds with strong orientation bonds. Such interaction occurs, for example, when polymer thickeners that substantially exceed the solubility of the components of the system are added to a mixture [14].

We can also assume that the observed deviation from the predicted viscosity of mixtures occurs possibly due to the energy state of the system, which can be estimated from the effective values [16].

The energy conditions of the system can be evaluated by calculation of the activation energy of viscous flow [7]:

$$E_a = R \times \ln\left(\mu_1 / \mu_2\right) / \left(\frac{1}{T_1} - \frac{1}{T_2}\right), \tag{8}$$

where E_a — activation energy, J/mol; R — universal gas constant, J/mol·K; μ_1 — viscosity of the system (cP) at a temperature T_1 (K).

Table 8 shows the results of calculation of the activation energy with the addition of tar from the primary cooler.

Table 8

The value of the activation energy of viscous flow, E_a, kJ/mol, with the addition of light tar

Temperature range, °C	Tar from primary cooler content, % w.					
	0.0	5.0	10.0	20.0	40.0	60.0
55–60	26.0	28.0	24.0	30.3	27.3	26.5
65–70	43.7	43.1	35.2	31.6	46.3	38.4
70–75	48.6	37.6	38.1	43.5	36.5	34.1
75–80	47.6	43.4	34.8	35.2	38.6	24.3
80	47.0	38.2	46.8	44.0	35.3	17.8

The minimum of activation energy of viscous flow corresponds to the amount of the additive at which the disintegration and the dissolution of the existing structures take place. In such systems, the speed of movement of each particle is less dependent on the position and speed of other particles. The increase in the value of E_a means moving in a more structured system condition. Less structured systems correspond to the light tar content of 5–20 % w., according to the data of Table 8.

The calculated value of the activation energy of viscous flow is confirmed non-random nature of the experimental data deviations from the simulated according to the formulas (2)–(5). In this area, there is certain lowering of viscosity from the calculated figures due to the destruction of the available ordered structures caused by introducing new tar components. Perhaps there is the increase of the dispersion phase volume in the existing structure of more dense and viscous heavy tar.

Minimum values of E_a in the temperature range of 55–60 °C while the addition of light tar of 10 % by weight are of practical significance for PGC washing technologies.

To take into account the non-ideality of the system an additional factor in the Arrhenius equation is sometimes introduced. The Grunberg-Nissan equation uses the principle of an ideal solution of mixture to evaluate the viscosity [14]:

$$\ln \eta_{1,2} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + \varepsilon x_1 x_2. \qquad (9)$$

In the equation (9) the constant ε is called the empirical coefficient of the interaction effect.

Fitting of the empirical coefficient of the Grunberg-Nissan equation was made in compliance with the maximum value of K and minimum value of δ. The results of calculation of the viscosity of the tar mixtures are presented in Table. 9.

Table 9

Calculated values of viscosity of the tar mixture and the empirical coefficient of the Grunberg-Nissan equation

Tempera-ture, °C	Tar from primary cooler content, % w.							ε
	0.0	5.0	10.0	20.0	40.0	60.0	100.0	
55	87.0	76.5	67.7	54.2	37.9	29.5	24.4	−1.3
60	75.4	68.8	62.9	53.0	39.1	30.1	20.2	−0.5
65	59.7	58.1	56.4	52.6	43.9	34.6	18.5	0.7
70	46.4	44.6	42.8	39.3	32.5	26.3	16.2	0.3
75	36.5	34.8	33.3	30.3	25.2	20.9	14.3	0.05
80	29.0	27.9	26.9	24.9	21.5	18.5	13.9	0.001

The Lederer-Roegiers equation adds an empirical parameter to account for differences in intermolecular cohesive energy between the components 1 and 2.

$$\ln \eta_{1,2} = \frac{x_1}{x_1 + \alpha x_2} \ln \eta_1 + \frac{\alpha x_2}{x_1 + \alpha x_2} \ln \eta_2. \qquad (10)$$

The results of calculation of the tar mixtures viscosity and α − parameter fitting are given in Table 10.

The results of the calculations of tar mixtures viscosity according to interaction of the mixing components show maximum of interaction coefficients in the temperature range

of 65–70 °C. The coefficient ε of the Grunberg-Nissan equation shows the elimination of the specific interaction of the mixed tars when the temperature rises to 75–80 °C.

Table 10

Calculated values of viscosity of the tar mixtures and α — parameter of the Lederer-Roegiers equation

Tempera-ture, °C	Tar from primary cooler content, % w.							α
	0,0	5.0	10.0	20.0	40.0	60.0	100.0	
55	870	786	71.4	60.0	44.7	35.2	24.4	1.6
60	75.4	63.4	54.7	43.4	31.7	25.9	20.2	2.8
65	59.7	50.6	44.2	35.8	27.1	22.8	18.5	3
70	46.4	39.2	34.4	28.2	22.1	19.1	16.2	3.5
75	36.5	32.0	28.7	24.2	19.4	16.9	14.3	3
80	29.0	25.4	23.0	20.0	16.9	15.4	13.9	4

Assessment of correlation of calculated and experimental data by the Grunberg-Nissan and Lederer-Roegiers equations is given in Table 11.

Table 11

The correlation coefficients and average relative deviation

Tempera-ture, °C	Equation			
	Grunberg-Nissan		Lederer-Roegiers	
	K	δ	K	δ
55	0.967	0.102	0.973	0.068
60	0.971	0.076	0.975	0.243
65	0.930	0.153	0.986	0.239
70	0.956	0.104	0.982	0.207
75	0.979	0.060	0.986	0.203
80	0.954	0.060	0.977	0.190
Average	0.960	0.093	0.980	0.192

The Grunberg-Nissan and Lederer-Roegiers equations are characterized by the fact that make theoretical basis in empirical relationships. It is believed that exactly the Lederer-Roegiers equation gives more accurate predictions of viscosity values for mixtures with large differences in viscosities. The correlation coefficients of this equation have maximal values in the whole investigated temperature range in the case of the viscosity prediction of the coal tar mixture. Thus, taking into account of intermolecular energy differences between cohesion of miscible tars allows to obtain the maximum correlation coefficient using the Lederer-Roegiers equation. The maximum for the interaction coefficient is noted in this equation at the temperature range of 65–70 °C. This indicates an increase in intermolecular cohesive energy when mixing tars from gas collecting main and primary cooler. It is possible due to occurrence of the orientation bonds between the highly polar compounds.

7. Conclusions

1. Measured values of coal tars from gas collecting main and primary cooler showed some reduced figures. The tars were obtained from the coking process of mainly imported coals. The investigated samples can be classified as high degree pyrolysis tar.

2. The resulting values of dynamic viscosity of tar mixtures can be used for adjusting the tar fluidity, for lowering viscosity when decanting and for preparing a wash liquid to dissolve the deposits. For example, to reduce the gas collecting main tar viscosity by adding of 40 % of tar from the primary cooler, in practice, it is sufficient to add 20 %.

3. The most applicable empirical model for prediction of coal tar mixture is the Refutas equation. An analysis of the equations that take into account deviations from the non-ideality of the system during mixing showed maximum values of coefficients of intermolecular cohesive energy. This is due to interactions of polar components and coal tars in the temperature range of 65–70 °C. These bonds are weakening at a temperature above 75–80 °C.

4. Mixing of coal tars from gas collecting main and primary cooler change the prevailing character of the interaction of macromolecules and dispersed structures of coal tar. Anomalous reduction in viscosity with the addition of 5–20 % of tar from primary cooler to tar from gas collecting main was revealed experimentally. Available empirical models and the ones taking into account the non-ideality of the system cannot predict the measured minimum of viscosity. Identified abnormal viscosity reduction corresponds to the minimum of activation energy of viscous flow. That corresponds to the value of the additive at which destruction and dissolution of the existing supramolecular structure probably take place.

Acknowledgment

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