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Optimal Conditions for Demetallization of the Heavy Fraction of Low-Temperature Coal Tar of Shubarkol Komir JSC in the Presence of "Coal Shale" Catalytic Additive

The optimal conditions for demetallization of the heavy fraction of coal tar from Shubarkol Komir JSC were determined by means of full factorial experiment. Optimal conditions for demetallization of the aforementioned fraction were found to be a proportion of "Coal shale" catalytic additive to the heavy fraction of coal tar with boiling point above 300 °C equal to 0.04, process temperature in the range of 420–430 °C, duration from 20 to 30 minutes and initial pressure between 3 and 5 MPa. Experiments conducted under these conditions demonstrated the demetallization rates of 87–89 %. Conversion of the heavy fraction of coal tar in hydrogen medium at pressure of 4.0 MPa and temperature of 420 °C was examined, with and without the use of the "Coal Shale" catalytic additive. The findings demonstrate that the incorporation of the "Coal Shale" catalytic additive is associated with a notable enhancement in the production of liquid hydrogenate, reaching up to 57 %. Atomic emission spectral analysis was used to investigate the content of rare and dispersed elements including Ge, Ga, Y, Yb, Zr, Nb the ash of the heavy fraction of coal tar and the "Coal shale" catalytic additive, as well as in the solid product of demetallization of the heavy fraction of coal tar using the catalytic additive. The results showed that the use of "Coal shale" as the catalytic additive leads to an increase in the content of Ga, Yb, Y elements by 3-3.8 times, and Zr — by 7.5 times compared to the initial heavy fraction of coal tar in the absence of the catalytic additive.

Keywords: full factorial experiment, coal shale, coal tar, rare trace elements, dispersed trace elements, ash, optimal conditions, demetallization, heavy fraction.

Introduction

It is evident that solid and heavy hydrocarbon raw materials, including coal, shale, heavy petroleum residues and coal tar represent a promising source of essential elements such as germanium, gallium, tungsten, nickel, molybdenum and rare earth elements [1–5]. Solid and heavy hydrocarbon raw materials, low-temperature coal tar and coal shale and their processing products are distinguished by an exceptional diversity of trace element composition [2]. Since to date, 84 elements of the periodic system have been identified in solid fossil fuels, of which most are trace elements, that is, their content does not exceed 0.1 %.

These sources, in addition to low-temperature coal tar and coal shale, stand out for their unique trace element composition. The latest research has revealed that solid fossil fuels contain [6, 7] up to 84 elements of the periodic table, the majority of which are classified as trace elements with a concentration below 0.1 %. This discovery highlights the potential of hydrocarbon raw materials as an alternative source for the extraction of rare metals, which could have a significant impact on the development of the metallurgical and chemical industries.

Oil shale is characterized by a high level of ash content, reaching 30-80 %, which limits their direct use in the energy and chemical industries. Nevertheless, they can be of great interest as catalytic additives and hydrogen donors for the processing of heavy hydrocarbons. The study [8] shows the possibility of using coal shale as hydrogen donors in the thermal dissolution of brown coal. A considerable quantity of hydrogen is present in oil shales, and the mineral part acts as a source of valuable trace elements [7].

Trace elements contained in solid and heavy hydrocarbon raw materials, in most cases, exceed or are commensurate with their quantitative purposefully extracted from ore raw materials [4]. The review [2] shows that work was carried out on the extraction of germanium from oil shale and coal tar fraction, and the inexpediency of extracting trace elements separately from complex and multicomponent raw materials has been established. In this regard, special attention is paid to technologies for concentrating metals [9-10] contained in oil shale and in the heavy fraction of coal tar into a solid phase by demetallization. Currently, the demetallization method is used for demetallization of heavy hydrocarbon feedstocks, in particular for heavy oil residues and heavy oils [10]. A review of the literature revealed that demetallization of solid fuels and coal tar is a relatively unsystematic process. Therefore, is crucial to identify the conditions that facilitate the concentration of trace elements in the solid phase through demetallization and to predict the most optimal methods for their processing. Additionally, it is essential to assess the feasibility of obtaining concentrates of these valuable metals.

The purpose of this study is to determine the optimal conditions for demetallization of the heavy fraction of low-temperature coal tar and coal shale from Shubarkol Komir JSC, and to investigate the impact of the “Coal Shale” catalytic additive on the qualitative and quantitative composition of the light and middle fraction obtained from the hydrogenation process.

Experimental

The heavy fraction of coal tar from Shubarkol Komir JSC, with boiling point above 300 °C, was selected for the study as a result of fractionation of low-temperature coal tar at atmospheric pressure. The elemental composition of the heavy fraction of coal tar of Shubarkol Komir JSC is presented in [11]. The catalytic additive used in this study was coal shale from Shubarkol Komir JSC (which will henceforth be referred to as the “Coal Shale” catalytic additive.

The original coal shale was subjected to grinding in a shek mill, then screened on *Sieve Shaker OBRK-SA, manufactured by Changzhou Oubeiruike Instrument and Equipment CO LTD, 2022*, with particles smaller than 0.1 and 0.1 mm, then stored in polyethylene bags.

The experimental conditions were selected on the basis of existing literature on catalytic hydrogenation of coal tar [10] and on the basis of our previous studies [12–15]. Demetallization experiments were performed in a high pressure reactor with a 0.3 L stirrer (PRC production). The initial hydrogen pressure is 3–5 MPa, the weight of the heavy fraction of coal tar with the catalytic addition of shale is 35–45 grams, the duration is from 20 to 60 minutes, the heating temperature is from 380 to 420 °C, the ratio of the catalytic addition of shale to the heavy fraction of tar with a boiling point above 300 °C varied in the range of 0.00–0.15.

During demetallization of the heavy fraction of coal tar with boiling point above 300 °C, Shubarkol Komir JSC obtained a hydrogenate, which was subjected to fractionation at atomospheric pressure: a light fraction of 100–200 °C and a middle fraction of 200–300 °C.

The solid phase of hydrogenation and the residue of hydrogenate fractionation with boiling point above 300 °C were ashed, and the concentration of 30 trace elements in the resulting ash was determined using the atomic emission spectral method. This method is based on the combustion of the sample in an electric arc discharge on a diffraction spectrograph 8 which is equipped with a multichannel analyzer of atomic emission spectra (MAES).

The results of the ash analysis were recalculated in relation to the heavy fraction of coal tar and the “Coal shale” catalytic additive, taking into account ash content by formula [16]:

$$C\left(\frac{g}{t}\right)=C_a * A/100, \tag{1}$$

where C is the concentration of element in the heavy fraction of coal tar and coal shale, C_a is the concentration of the element in ash, A is the ash content (%).

In order to study the possibility of using coal shale as the catalytic additive for demetallization of the heavy fraction of coal tar of Shubarkol Komir JSC, experiments were carried out without using the “Coal Shale” catalytic additive.

The experiment “Without catalytic additive” was carried out in a high-pressure reactor with stirring device at the temperature of 420 °C, initial hydrogen pressure of 4.0 MPa, and duration of 60 minutes.

Liquid products were also subjected to fractional distillation at atmospheric pressure with selection of the light fraction fraction 100–200 °C and the middle fraction 200–300 °C.

The individual chemical composition of the demetallization products of the heavy fraction of low-temperature coal tar of Shubarkol Komir JSC was determined using an Agilent 7890A gas chromatograph with an Agilent 5975C mass-selective detector. Column parameters Rxi-5ms: length — 30 m, diameter — 0.25 mm, column adsorbent thickness — 0.25 microns, column heating rate 8 °C/min, carrier gas — helium; gas pressure in the column 1.38×10^5 Pa; sample volume 2×10^{-4} cm^3; input mode — split, library — NIST08. The composition of the fractions was determined semi-quantitatively by peak area. The data were processed using the GSMSD Data Analysis program.

The elemental composition of the “Coal shale” catalytic additive comprising carbon, hydrogen and sulfur was determined using a CHNOS element analyzer Vario El Cube (Elementer Analysen System GmbH).

The texture characteristics of the catalyst additive were determined by physical nitrogen adsorption using a TriStar II 3020 (USA) instrument. The samples were heated under nitrogen current at 200°C for 1 hour before analysis. The BET specific surface area was calculated from the amount of nitrogen adsorbed in the range of relative pressures 0.05–0.30. The total pore volume was calculated from the amount of nitrogen adsorbed at a relative pressure close to unity ($P/P_0 = 0.874$), assuming that all available pores were filled with condensed nitrogen in the normal liquid state. The micropore volume was calculated using the t-method.

The composition and texture characteristics of the “Coal shale” catalytic additive are given in Table 1.

Table 1

Composition and textural characteristics of the catalytic additive

Sample	Ash content Ad	Content, wt.%			Textural characteristics		
		S	H	C	S_{sp}, m^2/g	V_{pores}, cm^3/g	$V_{micropores}$, cm^3/g
“Coal shale” catalytic additive	50–70	0.93	6.83	66.2	18.5348	0.053782	0.000485

In order to determine the optimal conditions for demetallization of the heavy fraction of coal tar of Shubarkol Komir JSC in the presence of the “Coal Shale” catalytic additive, we used a full factorial experiment (FFE). FFE is an experiment in which all possible, repeated combinations of factor levels are realized [17].

Results and Discussion

The effect of FFE on the degree of demetallization of the heavy fraction of coal tar with a boiling point above 300 °C and coal shale (y, %) was investigated. Coal shale is a source of trace elements, and also acts as the catalytic additive in the process of demetallization of mixture of the heavy fraction of coal tar and coal shale. The effects of four factors were studied: the ratio of the catalytic additive to the heavy fraction of coal tar above 300 °C (X_1) in the range of 0.00–0.15, temperature (X_2) 380–420 °C, process duration (X_3) 20–60 minutes, and initial hydrogen pressure (X_4) 3.0–5.0 MPa.

The FFE planning stages are as follows:

1. Factor coding;
2. Drawing up a matrix plan, $N = 2^4$, where N is the number of experiments, two levels of factor variation — upper and lower, factor coding +1, –1;
3. Checking the homogeneity of the dispersions of parallel experiments, their reproducibility;
4. Calculation of regression equation coefficients, their errors and significance;
5. Model adequacy testing.

The planning matrix with generating relationship $X_4 = X_1, X_2, X_3$ is shown in Table 2.

The levels of variable factors and their ranges are presented in Table 3.

Table 2

Half-replica from FFE with generating ratios $X_4 = X_1, X_2, X_3$, where X_4 is the initial hydrogen pressure factor

Experiment No.	Factors on a dimensionless scale					Degree of demetallization Y, %
	X_0	X_1	X_2	X_3	X_4	
1	+1	+1	+1	+1	+1	88.3
2	+1	–1	–1	+1	+1	64.0
3	+1	–1	+1	+1	–1	67.4
4	+1	+1	–1	+1	–1	56.7
5	+1	+1	+1	–1	–1	87.9
6	+1	–1	–1	–1	–1	66.2
7	+1	–1	+1	–1	+1	80.8
8	+1	+1	–1	–1	+1	75.0

Table 3

Levels of variable factors and intervals of variation

Level of factors	Factor code value				Natural values of factors			
	X_1	X_2	X_3	X_4	Ratio of tar fraction to the "Coal Shale" catalytic additive	T, ºC	τ, duration, min	P, initial hydrogen pressure, MPa
Basic level	0	0	0	0	0.11	400	40.0	3.0
Variation interval	1	1	1	1	0.04	20.0	20.0	2.0
Upper level	1	1	1	1	0.15	420	60.0	5.0
Lower level	–1	–1	–1	–1	0.11	380	20.0	3.0

Regression equation with coefficients:

$$\hat{y} = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 . \tag{2}$$

The coefficients of the regression equation were calculated using the following formulas:

$$b_0 = \tfrac{1}{8}\sum_1^8 x_0 y_i = 73.3 ; \tag{3}$$

$$b_1 = \tfrac{1}{8}\sum_1^8 x_1 y_i = 3.69 ; \tag{4}$$

$$b_2 = \tfrac{1}{8}\sum_1^8 x_2 y_i = 7.88 ; \tag{5}$$

$$b_3 = \tfrac{1}{8}\sum_1^8 x_3 y_i = 4.19 ; \tag{6}$$

$$b_4 = \tfrac{1}{8}\sum_1^8 x_4 y_i = 3.74 ; \tag{7}$$

$$\hat{y} = 77.3 + 3.69x_1 + 7.88x_2 + 4.19x_3 + 3.74x_4 . \tag{8}$$

The variability in the adequacy of the optimization parameter and the assessment of the significance of the coefficients in accordance with the Student's criterion [17] were calculated:

$$S_{var}^2 = \frac{\sum_1^3 \left(y_1^0 - \bar{y}_0\right)^2}{2} = 0.97 ; \tag{9}$$

$$S_{var} = 0.94 ; \tag{10}$$

$$S_{bj} = \frac{0.94}{\sqrt{8}} = 0.33 ; \tag{11}$$

$$t_0 = \frac{73.3}{0.33} = 222.08 ; \tag{12}$$

$$t_1 = \frac{3.69}{0.33} = 11.17\,; \tag{13}$$

$$t_2 = \frac{7.88}{0.33} = 23.84\,; \tag{14}$$

$$t_3 = \frac{4.19}{0.33} = 12.7\,; \tag{15}$$

$$t_4 = \frac{3.74}{0.33} = 11.33\,. \tag{16}$$

Three additional parallel experiments were conducted in the center of the matrix design (Table 2) and the following values of the degree of demetallization y, %, were obtained:

$$y_1^0 = 86.4\,; \tag{17}$$

$$y_2^0 = 88.3\,; \tag{18}$$

$$y_3^0 = 87.8\,; \tag{19}$$

$$\bar{y}_0 = \frac{\sum_{n=1}^{3} y_i^0}{3} = 87.5\,; \tag{20}$$

$$S_{res}^2 = \frac{\sum_{i=1}^{8}(y_i - \bar{y}_0)^2}{N - e} = \frac{(88.3 - 92.84)^2 + (64.0 - 69.6)^2 + (67.4 - 78.4)^2}{3} = 57.66\,. \tag{21}$$

We evaluate the significance of the coefficients in equation (8) according to the Student's criterion [17]. Since we have the number of parallel experiments is three, according to the tabulated values of the Student's criterion, for the significance level $n = 0.05$ and the number of degrees of freedom $f = 3–1 = 2$, then $t_r = 4.3$.

The adequacy of the obtained equation is checked by Fisher's criterion:

$$F = S_{res}^2 \Big/ S_{rep}^2 = \frac{57.7}{0.94} = 7.9\,. \tag{22}$$

The adequacy of the linear model was validated using F-test: $F_{calc} \le F_{tab}$, $F_{tab} = 19.3$.

Based on the matrix data and the regression equation, the following conclusions are made:

1. The greatest influence on the degree of demetallization of heavy fraction of coal tar above 300 °C in the presence of the “Coal Shale” catalytic additive is exerted by factors: X_2 — process temperature (°C), X_3 — process duration (min) and X_4 — initial hydrogen pressure.

2. The least effect on the degree of demetallization of the heavy fraction of the coal tar above 300 °C in the presence of the “Coal shale” catalytic additive is exerted by the factor X_1 — the ratio of the catalytic additive of oil shale to the heavy fraction of the coal tar above 300 °C.

The rate of molecular hydrogen consumption per unit of organic mass in the mixture was — 1.75 %. Hydrogen consumption was determined on the basis of the mixture, hydrogenate, solid residue and gas phase.

Thus, the optimal conditions for the hydrodemetallization process of the mixture: the ratio of the catalytic additive (“Coal shale”) to the heavy fraction of the coal tar above 300 °C is 0.04, the 420–430 °C temperature, the duration is 20–30 minutes, the initial pressure is 3–5 MPa. Carrying out the process under optimal conditions showed the degree of demetallization 87–89 %.

Table 4 presents the qualitative and quantitative composition of the light and middle fraction of hydrogenates obtained in the presence of the catalytic additive “Coal shale”, as well as in its absence.

Figure illustrates the component composition of the 100–200 °C light fraction and 200–300 °C middle fraction of the hydrogenate of the heavy fraction of coal tar of Shubarkol Komir JSC “Without catalytic additive” and using the “Coal shale” catalytic additive at the temperature of 420 °C, the initial hydrogen pressure of 4 MPa and the duration of 60 minutes.

The yield of liquid hydrogenate of the 100–200 °C light fraction without a catalytic additive is 5.2 %, while the yield of liquid hydrogenate of the 200–300 °C middle fraction is 9.0 %. The addition of the “Coal shale” catalytic additive, derived from the heavy fraction of coal tar with the boiling point above 300 °C, resulted in a significant increase in the yield of the liquid hydrogenate of the light fraction of 100–200 °C to 43.5 %, and a notable enhancement in the yield of the middle fraction of (200–300 °C) to 13.4 %.

Table 4

Individual chemical composition of light and middle hydrogenate fractions (experimental conditions: 420 °C, 60 min, 4 MPa, ratio 0.13)

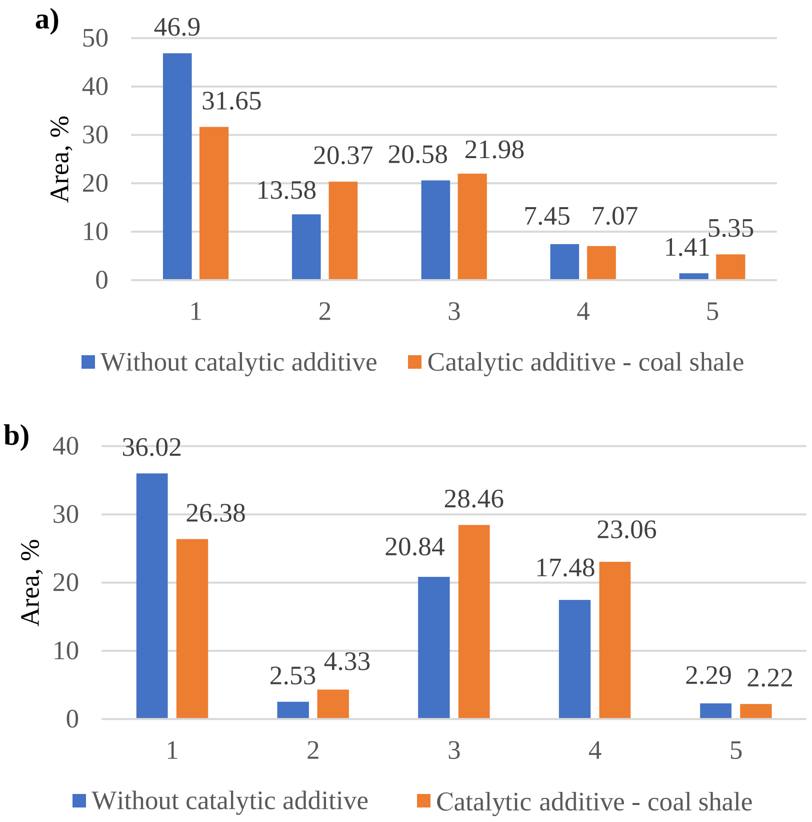
№	Class of compounds	Compounds	Area without and with catalytic additive “Coal shale”, %			
			100–200 °C Light fraction		200–300 °C Middle fraction	
			Without	With	Without	With
1	2	3	4	5	6	7
1	Paraffinic hydrocarbons	Pentane, 3-ethyl-2,2-dimethyl-	–	0.33	–	–
		Hexane, 2,5-dimethyl-	0.59	0.37	–	–
		Hexane, 3-ethyl-2,5-dimethyl-	–	0.46	–	–
		Heptane	2.09	–	–	–
		Heptane, 3-methyl-	2.88	–	–	–
		Heptane, 3-ethyl-2-methyl-	0.86	–	–	–
		Octane, 3-methyl-	0.33	–	–	–
		Octane, 2,3- dimethyl -	–	1.23	–	–
		Octane, 2,6-dimethyl-	0.75	0.87	–	–
		Octane, 3,5-dimethyl-	–	1.04	–	–
		Nonane, 2-methyl-	4.05	–	–	–
		Decane, 2,6,8-trimethyl-	5.0	–	–	–
		Decane, 2,6,7-trimethyl-	0.23	–	–	–
		Decane, 2,6,6-trimethyl-	–	4.72	–	–
		Decane, 2,5,9-trimethyl-	–	0.82	1.02	0.35
		Undecane, 3,6-dimethyl-	4.77	–	–	2.7
		Undecane, 4,6-dimethyl-	0.27	0.63	1.91	–
		Undecane, 2,5-dimethyl-	–	5.11	–	–
		Undecane, 2,6-dimethyl-	–	2.98	–	1.51
		Dodecane, 2,6,11-trimethyl-	13.2	–	3.54	–
		Dodecane, 2,7,10-trimethyl-	–	6.6	–	–
		Dodecane, 2-methyl-	0.26	–	–	–
		Pentadecane	3.06	3.02	3.83	3.34
		Heptadecane, 2,6-dimethyl-	–	2.08	–	–
		Heptadecane	5.1	–	2.75	11.9
		Eicosane	3.46	0,88	14.2	6.58
		Heneicosane	–	0.51	2.37	–
		Heptacosane	–	–	6.64	–
2	Aromatic hydrocarbons	Benzene, 1,3,5-triethyl-	0.27	–	0,51	–
		Benzene, 1-ethyl-2-methyl-	3.24	–	–	–
		Benzene, 1-methyl-3-propyl-	0,34	0.35	–	–
		Benzene, 1-methyl-4-propyl-	0.32	1.32	–	0.53
		Benzene, 1-ethenyl-4-methoxy-	–	–	–	0.32
		Benzene, (2-methyl-1-propenyl)-	0.62	–	–	–
		Benzene, 2-ethenyl-1,4-dimethyl-	0.28	–	–	–
		Benzene, 1-methyl-4-(1-methyl-2-propenyl)-	1.35	–	–	–
		Benzene, (2-ethenyl-1,4,4-trimethylpentyl)-	–	0.54	–	–
		Benzene, 1,1'-(1-methyl-1,2-ethanediyl) bis-	–	1	–	0.25
		Benzene, 1,3-dimethyl-	–	10.56	–	–
		Benzene, pentamethyl-	0.4	–	1	
		Benzene, (2-methyl-1-butenyl)-	–	–	–	0.46
		Benzene, (1-methyl-1-butenyl)-	–	–	–	0.78
		Benzene, (3-methyl-2-butenyl)-	–	–	–	0.27
		Benzene, 1-methoxy-4-(1-methylethyl)-	–	–	–	0.63
		Benzene, 1-methyl-4-(1-methylethenyl)	–	–	–	0.31
		Benzene, 2,4-diethyl-1-methyl-	–	–	–	0.36
		o-Isopropenyltoluene	–	–	–	0.42
		1,1'-Biphenyl, 2-methyl-	–	–	1.02	–

Continuation of Table 4

1	2	3	4	5	6	7
		Ethylbenzene	0.96	2,24	–	–
		o-Xylene	4.47	–	–	–
		Toluene	1.65	4.36	–	–
3	Phenols	Phenol	4.03	8.98	3.81	4.26
		Phenol, 2-methyl-	2.27	10.89	2.93	–
		Phenol, 3-methyl-	4.69	–		–
		Phenol, 4-methyl-	–	–	7.03	6.99
		Phenol, 2,3-dimethyl-	0.41	–	–	4.96
		Phenol, 4-ethyl-	0.60	–	–	–
		Phenol, 3,5-dimethyl-	5.41	–	–	–
		Phenol, 3,4-dimethyl-	–	–	–	0.9
		Phenol, 2,5-dimethyl-	0.44	–	–	4.18
		Phenol, 2,6-dimethyl-	–	–	–	1.05
		Phenol, 2-ethyl-	0.64	2.11	0.38	0.85
		Phenol, 3-ethyl-	–	–	4.81	–
		Phenol, 2-ethyl-5-methyl-	0.55	–	–	1.5
		Phenol, 2-ethyl-4-methyl-	–	–	–	2,54
		Phenol, 2,4,6-trimethyl-	1.59	–	–	–
		Phenol, 2,3,5-trimethyl-	–	–	0.17	–
		Phenol, 2,3,6-trimethyl-	–	–	–	0.92
		Phenol, 2-propyl-	–	–	1.42	–
		Phenol, 2-methyl-6-(2-propenyl)-	–	–	–	0.31
		Thymol	0.35	–	0.29	–
4	Polycyclic hydrocarbons	Naphthalene	0.87	–	–	1.69
		Naphthalene, 1-methyl-	2.25	3.06	–	4.41
		Naphthalene, 2-methyl-	–	–	2.95	–
		Naphthalene, 1-ethyl-	–	–	–	0.91
		Naphthalene, 2-ethyl-	0.25	0.28	0.96	–
		Naphthalene, 1,4-dimethyl-	2.11	–	1.6	1.21
		Naphthalene, 1,2-dimethyl-	–	0.51	–	–
		Naphthalene, 2,3-dimethyl-	–	0.41	1.92	3.02
		Naphthalene, 2,7-dimethyl-	–	–	1.47	–
		Naphthalene, 1,4,6-trimethyl-	0.27	0.33	–	3.24
		Naphthalene, 1,6,7-trimethyl-	1.09	–	–	–
		Naphthalene, 2,3,6-trimethyl-	–	–	4.23	–
		Naphthalene, 1,2,3,4-tetrahydro-5, 7-dimethyl-	–	0.32	–	–
		Naphthalene, 1,2,3,4-tetrahydro-1-methyl-	–	–	–	0.22
		Naphthalene, 1,2,3,4-tetrahydro-1,6,8-trimethyl-	–	–	–	0.25
		Naphthalene, 1-propyl-	–	–	0.37	0.25
		Naphthalene, 1,6-dimethyl-4-(1-methylethyl)-	–	–	–	0.55
		Fluorene	0.29	0.24	0.8	–
		Anthracene	0.32	0.38	–	–
		Anthracene, 2-methyl-	–	–	0.3	–
		Phenanthrene	–	–	2.12	1.03
		Phenanthrene, 2-methyl-	–	0.25	0.27	–
		Phenanthrene, 1-methyl-	–	–	–	0.47
		Phenanthrene, 1,7-dimethyl-	–	–	–	0.6
		Phenanthrene, 3,6-dimethyl-	–	–	0.21	–
		Phenanthrene, 2,3,5-trimethyl-	–	–	0.28	–
		Phenanthrene, 1-methyl-7-(1-methyl ethyl)-	–	0.21	–	0.3
		Azulene	–	1.08		
		1H-Indene, 2,3-dihydro-4,7-dimethyl-	–	–	–	0.58
		1H-Indene, 2,3-dihydro-1,1,5-trimethyl-	–	–	–	0.59
		1H-Indene, 2,3-dihydro-1,4,7-trimethyl-	–	–	–	0.92
		Fluorene	–	–	–	0.65
		9H-Fluorene, 2-methyl-	–	–	–	1.21
		2-Hydroxyfluorene	–	–	–	0.96

Continuation of Table 4

1	2	3	4	5	6	7
5	Heterocyclic hydrocarbons	Furan, 3-phenyl-	–	–	1.46	0.95
		Benzofuran, 2,3-dihydro-2-methyl-	0.51	–	–	–
		Benzofuran, 2-ethenyl-	0.47	–	–	–
		Dibenzofuran	–	–	0.45	0.42
		Dibenzofuran, 4-methyl-	0.43	–	0.38	0.34
		Benzenethanamine, N-(3-chloropropyl)-alpha-methyl-	–	2.04	–	–
		Benzenamine, 3-methyl-	–	1.57	–	–
		o-Toluidine	–	0.57	–	–
		5-aminoindole	–	0.43	–	–
		Pyridine, 3-ethyl-	–	0.49	–	–
		Pyridine, 3,4-dimethyl-	–	0.25	–	–
		Pyridine, 2,3-dimethyl-	–	–	–	0.3
		Quinoline, 2,6-dimethyl-	–	–	–	0.21



1 — Paraffin hydrocarbons; *2* — Aromatic hydrocarbons; *3* — Phenols;
4 — Polycyclic hydrocarbons; *5* — Heterocyclic hydrocarbons

Figure. Component composition of the 100–200 °C light fraction (*a*) and 200–300 °C middle fraction (*b*) of hydrogenate (420 °C, 60 min, 4 MPa, ratio 0.13)

The 100–200 °C light fraction, isolated from the products obtained by demetallization of the heavy fraction of coal tar on the “Coal Shale” catalytic additive, is characterized by a significantly lower content of marginal hydrocarbons compared to the light fraction isolated from the liquid product obtained by demetallization of the heavy fraction of coal tar “Without catalytic additive”.

Paraffin hydrocarbons of light fraction obtained in experiments “Without catalytic additive” and with the “Coal shale” catalytic additive are represented by homologues of heptane, octane, decane, undecane, dodecane, heptadecane and eicosane, but the content of higher paraffins decreases at demetallization on the “Coal shale” catalytic additive (Table 4).

o-Xylene (4.47 %) and toluene (1.65 %) are present in the 100–200 °C fraction separated from the hydrogenate during demetallization “Without catalytic additive”. In the same fraction, but obtained in the experiment with the “Coal shale” catalytic additive, o-xylene is absent, the toluene content increases to 4.36 % and Benzene, 1,3-dimethyl (10.56 %) is present in a significant amount.

The content of phenols slightly increases on the “Coal shale” catalytic additive, and the fraction consists of phenol (8.98 %), phenol, 2-methyl- (10.89 %) and phenol, 2-ethyl- (2.11 %).

The 100–200 °C fraction recovered in the “Without catalytic additive” demetallization process contains naphthalene, its derivatives, fluorene and anthracene, while in the 100–200 °C fraction obtained in the “Coal shale” catalytic additive demetallization process, polycyclic hydrocarbons are composed of naphthalenes, fluorene and anthracene, and azulene, and phenanthrenes are also present.

As illustrated in Table 4, the heterocyclic hydrocarbons in the first fraction, using the “Coal shale” catalytic additive, consist of amines and pyridines; during demetallization of heavy fraction of coal tar “Without catalytic additive” they are represented by oxygen-containing hydrocarbons.

Thus, the content of aromatic, heterocyclic compounds in the light fraction obtained on the “Coal shale” catalytic additive is higher than in the light fraction “Without catalytic additive”, which is associated with the conversion of saturated hydrocarbons and phenols into the corresponding aromatic and heterocyclic hydrocarbons (Fig.).

The 200–300 °C middle fraction, separated at fractionation of the hydrogenate of demetallization process of the heavy fraction of coal tar demetallization “Without catalytic additive” has significantly lower content of aromatic, polycyclic hydrocarbons and phenols in comparison with the second fraction obtained from the liquid product of demetallization with the use of the “Coal shale” catalytic additive.

The content of saturated hydrocarbons in the middle fraction of 200–300 °C in the presence of the “Coal Shale” catalytic additive is found to be lower than that of the middle fraction “Without catalytic additive”, with a decrease from 36.02 % to 26.38 %.

The content of aromatic hydrocarbons in the middle fraction extracted during demetallization of the heavy fraction of coal tar of Shubarkol Komir JSC in the experiment with the “Coal shale” catalytic additive is twice that of the experiment “Without catalytic additive”.

The “Coal shale” catalytic additive increases the yield of polycyclic hydrocarbons to 23 %, and phenols to 28.46 %; the content of heterocyclic compounds on the catalytic additive “Coal shale” practically does not change compared to the yield of heterocyclic hydrocarbons in the experiment “Without catalytic additive”.

Thus, the “Coal shale” catalytic additive promotes aromatization and the formation of polycyclic compounds from saturated hydrocarbons in both hydrogenate fractions.

The concentration of rare and dispersed trace elements in the ash of the heavy fraction of coal tar, in solid products and residues of demetallization of the heavy fraction of coal tar, taking into account ash content, is presented in Table 5.

Table 5

Concentration of rare and dispersed trace elements in the demetallization products of the heavy fraction of coal tar of Shubarkol Komir JSC

№	Composition of the mixture	Demetallization conditions	Trace element content, g/t					
			Ga	Ge	Yb	Y	Zr	Nb
1	Heavy fraction of coal tar	Initial mixture	0.5	0.4	0.1	1.2	1.2	0.7
2	Heavy fraction of coal tar	Initial mixture with the “Coal Shale” catalytic additive, ratio 0.13	1.8	<0.3	0.3	4.3	8.9	1.2
3	Solid phase of hydrogenate obtained by demetallization of heavy fraction of coal tar with the “Coal shale” catalytic additive	420 °C, 4 MPa, 60 minutes, ratio 0.13	1.6	<0.2	0.2	0.2	26.0	1.3
4	Solid residue obtained after fractionation of the heavy fraction of coal tar hydrogenate with the “Coal shale” catalytic additive	420 °C, 4 MPa, 60 minutes, ratio 0.13	≤0.1	<0.1	<0.04	<0.4	0.9	<0.3

According to the results obtained, the heavy fraction of coal tar is characterized by an insignificant content of rare and dispersed trace elements. When adding the “Coal shale” catalytic additive, the content of trace elements Ga, Yb, Y increases 3-3.8 times, and the content of Zr increases 7.5 times compared to the content of said trace elements in the initial fraction of coal tar without the “Coal shale” catalytic additive.

The content of trace elements in the solid residue obtained after fractionation of the heavy fraction of coal tar hydrogenate with the “Coal shale” catalytic additive is significantly lower than in the solid phase of the hydrogenate obtained by demetallization of the heavy fraction of coal tar with the “Coal shale” catalytic additive, which indicates the adsorption abilities of the “Coal shale” catalytic additive and the ability to obtain solid products with the high content of rare and dispersed trace elements.

Conclusions

Mathematical model of catalytic demetallization of the mixture of the heavy fraction of coal tar and shale is obtained. It has been found that coal shale effectively demetallizes the heavy fraction of coal tar and catalyzes the hydrogenation reactions of coal tar and affects the quantitative and qualitative change in the individual and group composition of the light and middle fractions of the hydrogenate. A high degree of demetallization of the heavy fraction of coal tar of Shubarkol Komir JSC is achieved while observing the temperature regime and the duration of the demetallization process. It should be noted that the ratio of the “Coal shale” catalytic additive to the heavy fraction of coal tar has a slight effect the degree of demetallization of the mixture of the heavy fraction of coal tar and coal shale.

It was found that the “Coal shale” catalytic additive increases the yield of liquid products of demetallization of the heavy fraction of coal tar four times compared to the demetallization of the heavy fraction of coal tar “Without catalytic additive”. Apparently, the “Coal shale” catalytic additive exhibits donor abilities and is a source of active hydrogen, activates molecular hydrogen to an atomic state, thereby explaining the high yield of the hydrogenate and the high degree of demetallization of trace elements.

The content of trace elements in the solid phase of the hydrogenate and in the solid residue obtained during fractionation of the hydrogenate, which increases in the presence of the “Coal shale” catalytic additive both in the initial heavy fraction of coal tar and the solid residue of demetallization of the heavy fraction of coal tar, has been established. It is shown that the total content of trace elements Ga, Ge, Y, Yb, Zr, Nb in the solid phase of demetallization of the heavy fraction of coal tar is 1.8 times higher than in the initial mixture of the heavy fraction of coal tar and the “Coal shale” catalytic additive.

The obtained results can be used when selecting alternative methods for processing heavy and solid hydrocarbon materials with the objective of concentrating valuable trace elements and predicting the composition of the resulting liquid products.

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Conflicts of Interest

The authors declare no conflicts of interest.

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