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Cavitation Extraction of Phenols form Coal Tar

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Abstract—The results of the chromatographic analysis of coal tar for the concentrations of phenols and their derivatives are given. It was shown that coal tar from AO Sary-Arka Spetskoks is characterized by a high concentration of phenols, which serve as a source material for organic synthesis. The possibility of applying ethanol and cavitation treatment to the extraction of phenols from the coal tar was established. The following optimum process conditions were found: ethanol concentration, 55–70%; duration, 5–7 min; the ratio ethanol : tar = 2 : 1; and the temperature of the cavitation treatment of primary coal tar, 333 K. A diagram for the extraction-cavitation treatment of primary coal tar was proposed.

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It is well known that primary coal tar is a valuable petrochemical raw material, from which a wide range of chemical substances can be obtained. Note that the fundamentals of the chemical processing by primary coal tar are under development in many countries such as the United States, Germany, France, Japan, Russia, and the Republic of Kazakhstan. The extraction of phenols, nitrogen bases, and naphthalene from the phenol fractions of coal tar is one of the main directions of coal tar processing.

The presence of 18–24% total phenols is a constraint on the industrial use of tar from Sary-Arka Spetskoks; however, at the same time, it opens prospects for their extraction for use in the chemical industry. The tar with removed phenols can be used for further conversion into motor or boiler fuel and also for the production of different organic raw materials. Phenols are used in industry for the manufacture of phenol–formaldehyde resins. Large quantities of phenol are converted into cyclohexanol, which is necessary for the production of synthetic fiber.

As a rule, the low-boiling fractions (initial boiling point, 300°C) are subjected to dephenolization in actual practice: the gasoline–ligroin and kerosene fractions of primary tar; the phenol and naphthalene fractions of coal tar; and the fraction (60–240°C) of brown coal hydrogenate [1–3]. Extraction with polar solvents, most frequently, with methanol and its aqueous solutions, and also extraction with an alkali with the conversion of phenols into phenolates are used in by-product-coking industry for the extraction of phenols. The latter method results in the most complete and selective extraction of phenols, but it is connected with the irreversible consumption of large amounts of an expensive alkali. The industrially used causticization of soda solutions obtained after the decomposition of phenolates leads to significant expenditures and the formation of large volumes of wastewater.

EXPERIMENTAL

Crude tar from AO Sary-Arka Spetskoks (Karaganda, the Republic of Kazakhstan), whose characteristics are given in Table 1, was used as a raw material for the extraction-cavitation treatment.

Table 1. Characteristics of coal tar

Characteristic	Value
Density ρ_4^{20}, kg/m^3	1042
Fraction composition, wt %	
initial boiling point 180°C	6.2
180–230°C	14.8
230–270°C	31.1
270–300°C	35.2
above 300°C	12.7
Elemental composition, wt %	
C	91.1
H	5.5
S	0.35
N	1.4
O (by difference)	1.65

Table 2. Concentrations of phenols in the tar of AO Sary-Arka Spetskoks

No.	τ_e (elution time), min	Compound	Relative concentration, %
1	2.173	Phenol	2.003
2	2.734	2-Methylphenol	2.144
3	2.895	4-Methylphenol	3.479
4	3.274	2,6-Dimethylphenol	0.488
5	3.504	2-Ethylphenol	0.407
6	3.627	2,4-Dimethylphenol	2.400
7	3.820	3-Ethylphenol	2.932
10	3.954	2,3-Dimethylphenol	0.240
11	4.109	3,4-Dimethylphenol	0.735
12	4.291	2,4,6-Trimethylphenol	0.339
13	4.499	2-Ethyl-5-methylphenol	0.764
14	4.553	3,4,5-Trimethylphenol	0.297
15	4.628	2-Ethyl-6-methylphenol	0.570
16	4.868	2-Ethyl-6-methylphenol	0.875
17	4.991	2,4,5-Trimethylphenol	0.243
18	5.045	2,3,5-Trimethylphenol	0.497

The prepared test sample of coal tar ($V = 150$ mL) was subjected to rotary-pulsation cavitation; the rate of stirring corresponded to a value of 3. The duration of the cavitation treatment was 1 and 5 min. After the cavitation treatment, we measured the kinematic viscosity of coal tar at temperatures of 313, 333, and 353 K. A mathematical method of experimental design was used for the optimization of cavitation treatment [4–7]. Then, analysis was performed to determine the elemental and functional-group compositions of the initial and processed coal tar samples in accordance with published procedures [8, 9].

The chemical composition of tar fractions was determined by gas chromatography–mass spectrometry (GC–MS) on an Agilent HP 5890/5972 MSD chromatograph (the United States) under the following conditions: column, DB-5, 30 m × 0.25 mm; phase film thickness, 0.5 μm; injector, 250°C; column oven temperature, 50°C for 4 min, 50–150°C at 10 K/min, 150–300°C at 10 K/min, and 300°C for 4 min; gas, helium at a flow rate of 0.8 mL/min; and injected sample volume, 20 μL. The mass spectra of the raw material components and the resulting products were measured in the total ion current mode. The experimental mass spectra were compared with the library mass spectra (NIST98 library).

The cavitator used in the treatment of petroleum and oil products, coal tar, and other raw materials had the following parameters: NMSH 5-25-4.0/25 pump

Liquid flow rate	4.0 m^3/h
Operating temperature	70°C
Output pressure	25 atm

Model VKNT 4.0/01-D

Liquid flow rate	4.0 m^3/h
Operating temperature	250°C
Operating pressure	30 atm

The cavitator used produces an axial low-pressure region, which is necessary for the break of liquid continuity and the appearance of a vapor–gas phase at a temperature of 25°C. A zone of the almost complete boiling of liquid with the formation of bubbles and cavities filled with vapor is formed in the centerline. In the region of atmospheric pressures, the collapse of vapor–gas bubbles will further occur with the formation of powerful cavitation zones. The above device makes it possible to conduct the cavitation treatment of different liquids; in this case, the maximum flow rate is 4 m^3/h at a pressure of 25 atm. However, the liq-

Table 3. Test factor levels

Factor	Level		
	minimum	medium	maximum
A is ethanol concentration, %	40	55	70
B is duration, min	5	10	15
C is the ratio of ethanol to primary coal tar	1	1.5	2.0
D is temperature*, K	313	323	333

* Temperature at which the cavitation treatment of tar was performed.

uid flow rate through a vortex cavitator will decrease with increasing viscosity.

RESULTS AND DISCUSSION

Extraction with the aqueous solutions of alcohols is convenient due to simpler solvent recovery and, in a number of cases, more preferable although the degree of extraction of phenols is lower than that in the alkaline method [20]. Taking into account difficulties related to the use of methanol (high toxicity), we performed studies with the replacement of it by ethanol in the process of phenol extraction from the tar of AO Sary-Arka Spetskoks. We used extractants based on the aqueous solutions of commercial ethanol with concentrations of 40 and 70% for the extraction of phenols. The composition of phenols in the initial coal tar was determined by GC–MS analysis (Table 2).

From an analysis of published data, it is well known that phenols are mainly extracted from the light fractions of coal tar; however, there are no published data on the extraction of phenols from primary coal tar with the use of lower alcohols. The effects of different factors on the extraction of phenols were determined with the use of multifactor experimental design [4–7]. For this purpose, we investigated the influence of four main factors (Table 3). Table 4 shows the orthogonal array of experimental design:

$$\overline{A_1} = 1/4(Y_{E_1} + Y_{E_2} + Y_{E_3} + Y_{E_4}) = 76.4, \tag{1}$$

$$\overline{A_2} = 1/4(Y_{E_5} + Y_{E_6} + Y_{E_8} + Y_{E_9}) = 74.6, \tag{2}$$

$$\overline{A_1} - \overline{A_2} = 76.4 - 74.6 = 1.8 > 0, \tag{3}$$

$$\overline{B_1} = 1/4(Y_{E_1} + Y_{E_2} + Y_{E_5} + Y_{E_6}) = 76.6, \tag{4}$$

$$\overline{B_2} = 1/4(Y_{E_3} + Y_{E_4} + Y_{E_7} + Y_{E_8}) = 74.4, \tag{5}$$

$$\overline{B_1} - \overline{B_2} = 22 > 0, \tag{6}$$

$$\overline{C_1} = 1/4(Y_{E_1} + Y_{E_3} + Y_{E_5} + Y_{E_7}) = 73.4, \tag{7}$$

$$\overline{C_2} = 1/4(Y_{E_2} + Y_{E_4} + Y_{E_6} + Y_{E_8}) = 77.6, \tag{8}$$

Table 4. Experimental design array for the extraction of phenols from primary coal tar

No.	*A*	*B*		*C*			*D*	Y_E, %
	1	2	3	4	5	6	7	
1	1	1	1	1	1	1	1	71.5
2	1	1	1	2	2	2	2	79.4
3	1	2	2	1	1	2	2	76.2
4	1	2	2	2	2	1	1	78.5
5	2	1	2	1	2	1	2	75.4
6	2	1	2	2	1	2	1	80.1
7	2	2	1	1	2	2	1	70.4
8	2	2	1	2	1	1	2	72.3
I*f*	305.6	306.4		293.5			300.5	
II*f*	298.2	297.4		310.3			303.3	
$\bar{\text{I}}$ = I*f*/4	76.4	76.6		73.4			75.1	
$\overline{\text{II}}$ = II*f*/4	74.6	74.4		77.6			75.8	
$\bar{\text{I}} - \overline{\text{II}}$	1.8	2.2		–4.2			–0.7	

Note: Y_E is the degree of phenol extraction from primary coal tar; *A*–*D* are factors affecting the degree of phenol extraction from tar.

Table 5. Mutual effects of factors on the degree of phenol extraction from primary tar

Factors	*A*	*B*	*AB*	*C*	*AC*	*BC*	*D*
	1	2	3	4	5	6	7
I*f*	305.6	–	293.6	–	300.2	297.7	300.5
	–	306.4	–	293.5	303.7	–	303.3
II*f*	298.2	–	233.9	–	–	–	–
	–	297.4	–	310.3	–	–	–
$\frac{\mathrm{I}f - \mathrm{II}f}{4}$	1.9	2.3	–4.15	–4.2	–0.9	–0.2	–0.7

Table 6. Concentrations of phenols in tar after the extraction treatment of primary coal tar with 70% ethanol

No.	τ_e, min	Compound	Relative concentration, %
1	2.173	Phenol	0.595
2	2.734	2-Methylphenol	0.685
3	2.900	4-Methylphenol	0.884
4	3.633	2,4-Dimethylphenol	1.243
5	3.825	2-Ethylphenol	0.750
6	4.499	2-Ethyl-6-methylphenol	0.457
7	4.633	2-Ethyl-5-methylphenol	0.205
8	4.692	2,3,5-Trimethylphenol	0.293

$$\overline{C_1} - \overline{C_2} = 2.2 > 0, \tag{9}$$

$$\overline{D_1} = 1/4(Y_{E_1} + Y_{E_4} + Y_{E_6} + Y_{E_8}) = 75.1, \tag{10}$$

$$\overline{D_2} = 1/4(Y_{E_2} + Y_{E_3} + Y_{E_5} + Y_{E_8}) = 75.8, \tag{11}$$

$$\overline{B_1} - \overline{B_2} = \overline{\mathrm{I}_2} - \overline{\mathrm{II}_2} = 2.2, \tag{12}$$

$$\overline{C_1} - \overline{C_2} = \overline{\mathrm{I}_4} - \overline{\mathrm{II}_4} = -4.2, \tag{13}$$

$$\overline{D_1} - \overline{D_2} = \overline{\mathrm{I}_7} - \overline{\mathrm{II}_7} = -0.7. \tag{14}$$

The mutual effects of factors $A \times B$, $A \times C$, and $B \times C$ on the degree of phenol extraction from primary tar have the form

$$\begin{aligned} A \times B &= 1/4(Y_1 + Y_2 + Y_7 + Y_8) \\ &\quad - 1/4(Y_3 + Y_4 + Y_5 + Y_6) \\ &= 1/4(71.5 + 79.4 + 70.4 + 72.3) \\ &\quad - 1/4(76.2 + 78.5 + 75.4 + 80.1) = -4.1, \end{aligned} \tag{15}$$

$$\begin{aligned} A \times C &= 1/4(Y_1 + Y_3 + Y_6 + Y_8) \\ &\quad - 1/4(Y_2 + Y_4 + Y_5 + Y_7) \\ &= 1/4(71.5 + 76.2 + 80.1 + 72.3) \\ &\quad - 1/4(79.4 + 78.5 + 75.4 + 70.4) = -0.9, \end{aligned} \tag{16}$$

$$\begin{aligned} B \times C &= 1/4(Y_1 + Y_4 + Y_5 + Y_8) \\ &\quad - 1/4(Y_1 + Y_3 + Y_6 + Y_7) \\ &= 1/4(71.5 + 78.5 + 76.4 + 72.3) \\ &\quad - 1/4(71.5 + 76.2 + 80.1 + 70.4) = -0.2 \end{aligned} \tag{17}$$

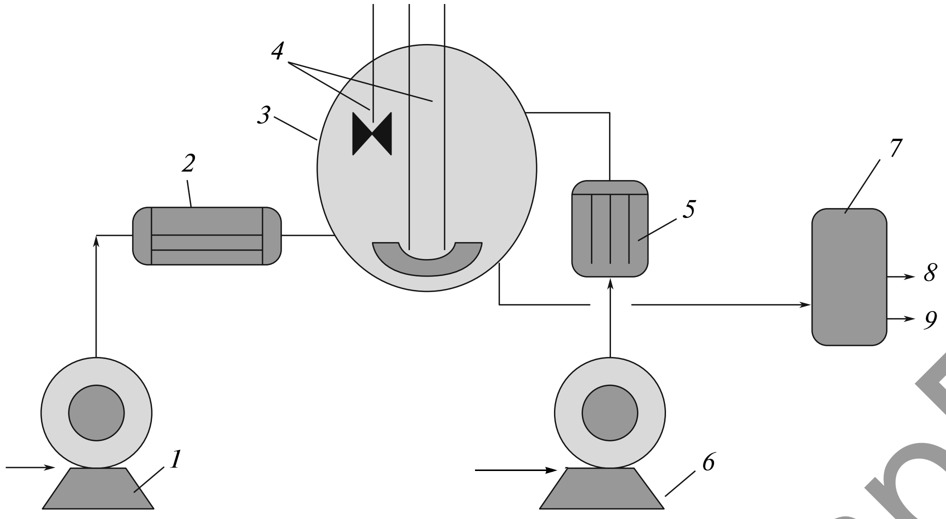
and they are summarized in Table 5.

An analysis of the results given in Table 5 shows that factor *C* and two factors *A* and *B* exert predominant effects (4.2 and 4.15, respectively) on the degree of phenol extraction from the primary coal tar. Thus, the investigated factors can be arranged in the following order with respect to their influence on the degree of phenol extraction from tar:

$$C > B > A > D.$$

As a result of the experiments, we determined a number of factors and found optimum conditions for the extraction of phenols from primary coal tar with the use of ethanol. The optimum conditions of the extraction of phenols from primary coal tar are the following: ethanol concentration, 55–70%; duration, 5–7 min; ethanol : tar ratio, 2 : 1; and the temperature of the cavitation treatment of primary coal tar, 333 K.

From the results of laboratory tests, it follows that a 70% aqueous solution of ethanol in a 2 : 1 ratio to tar or a 55 % aqueous solution of ethanol in the extrac-



Process flow chart of the extraction of phenols from the tar of AO Sary-Arka Spetskoks: (*1*, *6*) pumps, (*2*) heat exchanger, (*3*) extractor, (*4*) anchor and paddle stirrers, (*5*) vortex cavitation heater, (*7*) collector, (*8*) extract outlet, and (*9*) phenol-free tar outlet.

tion-cavitation treatment of tar followed by the separation of the mixture exhibited the best extraction properties.

In connection with the above, we determined two promising methods for the extraction of phenols from the tar of AO Sary-Arka Spetskoks: (1) extraction with a 70% solution of ethanol and (2) an extraction-cavitation method. The figure shows the process flow chart of the extraction of phenols from the coal tar of AO Sary-Arka Spetskoks.

The initial tar (V = 45 L) was supplied to heat exchanger *5* with pump *6*; it was heated to 60°C in the heat exchanger and arrived at the top of extraction column *3* (with a volume of 100 L). The extractant (V = 45 L; a 70% aqueous solution of commercial ethanol) was supplied to the bottom of the extraction column with pump *1* through heat exchanger *2* heated to 60°C. For the better contact of the tar with the extractant, the mixture was intensely stirred with anchor and paddle stirrers *4* for 10–15 min.

The contact of components occurred in the extractor due to the stirring and countercurrent of the tar and the extractant, as a result which to 80% of phenols from the tar was extracted and passed into the aqueous ethanol solution. After 15 min, the extraction mixture passed into collector *7*, where the mixture was separated. Then, the extract passed to a rectifying still through drain hole *8*; in the rectifying still, the extractant was distilled at a temperature of 90–100°C and returned to the process. The purified tar from the bottom part of the settler entered a collector through drain hole *9*. The concentration of phenols in the extract increased after the removal of the extractant. According to GC–MS analysis data, the concentration of phenols decreased from 18.83 to 5.11% or by

Table 7. Concentrations of phenols in tar after the cavitation-extraction treatment of primary coal tar

No.	τ_e, min	Compound	Relative concentration, %
1	2.162	Phenol	0.538
2	2.723	2-Methylphenol	0.303
4	3.124	2-Methoxypheno	0.362
3	2.889	4-Methylphenol	0.654
4	3.622	2,4-Dimethylphenol	0.621
5	3.814	3-Ethylphenol	0.269
6	4.488	2-Ethyl-5-methylphenol	0.397
7	4.622	2-(1-Methylethyl)phenol	0.281
8	4.868	2-Ethyl-6-methylphenol	0.527
9	5.034	2,3,5-Trimethylphenol	0.817

Table 8. Concentrations of light phenols in the extract after the cavitation-extraction treatment of primary coal tar

No.	τ_e, min	Compound	Relative concentration, %
1	2.2	Phenol	9.4
2	2.7	2-Methylphenol	7.4
3	2.9	4-Methylphenol	17.0
4	3.1	2-Methoxyphenol	0.4
5	3.3	2,6-Dimethylphenol	1.2
6	3.5	2-Ethylphenol	1.8
7	3.6	2,4-Dimethylphenol	8.6
8	3.8	3-Ethylphenol	10.6
9	3.9	2,3-Dimethylphenol	1.1
10	4.1	3,4-Dimethylphenol	1.8
11	4.3	2,4,6-Trimethylphenol	0.9
12	4.4	2-Propylphenol	0.2
13	4.5	2-Ethyl-5-methylphenol	2.4
14	4.53	3,4,5-Trimethylphenol	0.6
15	4.6	2-(1-Methylethyl)phenol	2.5
16	4.9	2-Ethyl-6-methylphenol	3.5
17	4.9	2,4,5-Trimethylphenol	0.7
18	5.0	2,3,5-Trimethylphenol	0.8
19	5.5	3,4-Diethylphenol	0.8
20	5.7	2-(1-Methylpropyl)phenol	0.5

76% on an initial tar basis. Table 6 summarizes the component composition of phenols.

For extraction-cavitation treatment, 40 L of the initial tar was supplied to heat exchanger *5* with pump *6*; it was heated to 60°C in the heat exchanger and supplied to the upper part of 0.1-m^3 extraction column *3*; 40 L of the extractant (a 40% aqueous solution of commercial ethanol) was supplied to the bottom part of the extraction column with pump *1* through heat exchanger *2* heated to 60°C. For the better contact of the tar with the extractant, the mixture was intensely stirred with anchor and paddle stirrers *4* for 10–15 min; thereafter, it was supplied to the VKNT-4.0/01-D vortex cavitation heater of fuel with the NMSh 5-25-4.0/25 pump from OOO KPM in Chelyabinsk (Russia).

After the extraction-cavitation treatment, the concentration of phenols in the tar decreased from 18.83 to 4.77%. Table 7 summarizes the component composition of phenols. After the cavitation treatment, the extraction mixture was poured into collector *7*, where the mixture was separated. Then, the extract passed into a rectifying still through drain hole *8*; in the rectifying still, the extractant was distilled at a temperature of 90–100°C and returned to the process. The concentration of light phenols in the extract after the removal of the solvent was 78.2%, and the concentration of total phenols was 84.3% (Table 8) [11, 12].

Analyzing the experimental results given in Tables 5–7, note that the amount of phenol extracted into an aqueous solution of ethanol substantially depends on the cavitation treatment of primary coal tar because the wave process favorably affects the process of the dissolution of total phenols in the aqueous solution of ethanol.

CONCLUSIONS

Thus, we found optimum conditions for the extraction of total phenols from primary coal tar with the use of an aqueous solution of ethanol and demonstrated the prevailing factors (ethanol concentration, duration, and ethanol to primary coal tar ratio) affecting the process of extraction. We proposed a flow chart for the extraction of phenols by the preliminary cavitation treatment of primary coal tar.

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