

chemical analysis, IR-spectroscopy and Chromato-Mass Spectrometry [9] are provided. The obtained data on the composition of CT group fractions confirmed the appropriateness of using coal tar as a potential raw material for producing valuable aromatic hydrocarbons, their mixtures and commercial chemicals based on them. In this paper we study the application of ozonation and hydrogenation processes for intensification of processing of semi-coking coal tar of the Shubarkol Deposit with increasing yield of light distillate fractions and valuable chemical products.

## 1. Experimental procedure

Coal tar of Sary-Arka Spetskoks JSC (Karaganda city, Republic of Kazakhstan) and a distillation residue with the boiling point above 320 °C of oil from the Kumkol Deposit (Republic of Kazakhstan), taken in a ratio of 1:1, were used as raw materials. The density of coal tar at 20 °C was 1.071 g/cm<sup>3</sup>; water content 3.4%; polyaromatic hydrocarbons 60.0%; sulphur 0.35%; fractions boiling out at temperatures of up to 180 °C 2.4%; 180–330 °C 19.0%; above 330 °C 78.6%. The oil residue had the following characteristics: density at 20 °C 0.8077 g/cm<sup>3</sup>; viscosity 969 mm<sup>2</sup>/s; content, wt. %: paraffins 14,73; asphaltenes 1,52; pitches 8,2; elemental composition, wt. %: C 83,85; H 11,27; S 1,81; N 0,80; O 2,27. The chemical composition of the non-hydrochemical distillate fractions of the semi-coking coal tar from the Shubarkol Deposit shows that they include alkyl derivatives of aromatic hydrocarbons with 1–4 aromatic rings. Benzene and its methyl, ethyl and propyl derivatives were identified as part of the distillates with a boiling point up to 180 °C. In the fraction with a boiling point of 180–320 °C traces of these compounds were found (<0.1 wt%).

Chemically this fraction mainly consists of trimethyl and ethyl derivatives of benzene, phenol and its methyl derivatives. In addition, indene, naphthalene and their alkyl derivatives, together with small quantities of biphenyls, acenaphthenes and dibenzofuran, were identified in its composition. The pattern of distribution of S-, N-, O heteroatoms as a part of aromatic structures of Shubarkol coal tar varies. Nitrogen is a part of both six-membered and five-membered rings, oxygen is a part of hydroxyl group and five-membered ring, and sulfur is only a part of five-membered ring (thiophene fragment). Ozonation of the coal tar was conducted in a laboratory ozonator PV-5 at 20 °C and atmospheric pressure. The traditional method for producing ozone by using DBD arrangements with a gas gap was applied in the ozonator. Ozone synthesis was performed using dehydrated air by short cycle non-heating air

adsorption in an airlift reactor with continuous feeding of ozone-air mixture (2.16 mol.% ozone) at the rate of 0.25 ml/min. The ozonator was cooled by the ambient air.

The duration of ozonation was 30, 60, and 90 min. Experiments on hydrofining of coal tar were carried out in the conditions of laboratory high-pressure unit with a hollow reactor with the volume of 0.25 dm<sup>3</sup> and an agitator in the presence of nanoheterogeneous molybdenum disulfide catalysts (Mo content 0.025% and 0.05%), received in situ in coal tar with the addition of sulfiding chemical - elemental sulfur in the amount of 0.03 wt% for raw material- in the first case, and without the addition of sulfur - in the second case. Catalyst sulphiding with 0.05% of Mo was conducted with the use of sulfur contained in coal tar. Catalysts preparation was carried out by adding aqueous solution of ammonium heptamolybdate (3.0 wt% of raw material) to the coal tar and by dispersing the produced mixture in a homogenizer at 130 °C and plate rotation speed of 1500 rpm. Then the mixture of coal tar and catalyst was heated up to 70–80 °C and loaded into the reactor, which was previously blown out with argon and filled with hydrogen at initial pressure of 2–3 MPa. Heating of reactor was switched on by removable electric furnace, and at reaching 150 °C - by the agitator. The temperature was measured by thermocouple converter and it was automatically maintained with an accuracy of ± 2 °C. The working pressure of hydrogen was 5.0 MPa, temperature 350–450 °C, reaction time 15 min.

The individual chemical composition of distillate fractions of the initial coal tar (Table 1) was determined by the Chromato-Mass Spectrometry method using the Agilent chromatograph (USA), model 6890, with a mass-selective detector, model 5973, with ionization by electronic impact (70 eV) under the following conditions: column - HP-5MS quartz capillary column (25 m × 25 mm, phase film thickness - 0.25 μm); temperature of the injector - 280 °C, temperature of the interface - 290 °C; initial and final temperature of the thermostat - 35 and 280 °C accordingly; Exposure of the column heating oven at the initial temperature - 1.0 min.; the temperature of the column heating oven was changed at a speed of 10° C / min; gas carrier - helium; the injection volume is 0.2 mL. Samples were injected with 1:40 split ratio mode. Registration of mass spectra of raw materials components and products was carried out in the total ion current mode. The received mass spectra were compared with library mass spectra (libraries NIST98, WILEY7n, PMW TOXR, etc.)

The quantitative composition of the fractions is calculated by the method of normalization. Data on composition of coal tar are

**Table 1**

Results of hydrofining of coal tar (5.0 MPa, τ = 15 min; ozone feeding rate 0.25 ml/min, nanoheterogeneous molybdenum disulfide catalyst; high pressure laboratory unit).

Mo content in catalyst per raw material, wt%	Temperature, °C	Yield of distillate fractions c with boiling point °C, wt%		Total yield of distillate fractions, wt %	Gas generation, wt %.	Residue, wt %	Losses, wt %
		< 180	180–320				
Ozonation time 0 min 0,025% Mo + 0,03% S	350	5,3	17,6	22,9	43,0	16,2	17,9
	400	7,8	32,7	40,5	36,3	15,7	7,5
	450	10,3	15,6	25,9	39,9	19,3	14,9
Ozonation time 30 min 0,025% Mo + 0,03% S	350	6,2	18,5	24,7	46,1	14,5	14,7
	400	12,4	32,4	44,8	25,1	24,8	5,3
	450	14,3	20,6	34,9	40,8	13,1	11,2
Ozonation time 60 min 0,025% Mo + 0,03% S	350	8,4	19,6	28,0	46,0	10,2	15,8
	400	14,8	33,4	48,2	32,8	13,0	6,0
	450	12,3	20,5	32,8	39,0	14,3	13,9
Ozonation time 90 min 0,025% Mo + 0,03% S	350	5,5	18,5	24,0	49,0	11,2	15,8
	400	11,8	32,4	44,2	26,8	12,3	16,7
	450	11,4	20,6	32,0	37,0	13,3	17,7