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Hydrofining of ozonized coal tar in the presence of molybdenum-sulphide catalysts

Zh.K. Kairbekov [a,c], N.T. Smagulova [a,c], A.S. Maloletnev [b], N.A. Abik [a,b,c], Y.B. Otynshiyev [a,b,c]

[a] RSE Al-Farabi Kazakh National University, Almaty 050040. Republic of Kazakhstan
[b] Moscow Mining Institute NITU MISiS, Moscow 119049. Russia
[c] State Enterprise Research Institute of New Chemical Technologies and Materials, Almaty 050040. Republic of Kazakhstan

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ABSTRACT

Hydrofining in the presence of nanoheterogeneous molybdenum-sulphide catalysts and low-temperature ozonation of the non-dehydrated semi-coking coal tar from the Shubarkol Deposit was conducted. As a result of ozonization of coal tar (CT), the conversion of its component composition with the increased yield of aromatic hydrocarbons and significant reduction of sulfur compounds, toxic heterocyclic and carcinogenic polycyclic arenes was achieved, which contributes to the treatment and improvement of the quality of tar products.

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The majority of researches in the field of coke chemistry are focused on intensification of coal tar (CT) processing since their chemical composition and physical properties exert a significant influence on the quantity and quality of distillate fractions, pitches and other coke-chemical products. In the paper [1] for increasing the yield and improving the quality of marketable products, a new concept of coal tar recovery is proposed, which consists in its hydrogenation refining under the pressure of hydrogen up to 5 MPa (without preliminary distillation of the tar) in the presence of a nanoheterogeneous molybdenum sulfide catalyst and its own hydrogen donor (technical tetralene), produced by hydrogenation of the fraction with boiling points 180–230 °C. In order to significantly simplify the technology of oil refining, increase the yield of oil products and improve their quality, a new technology has been developed [2], which lies in the fact that crude oil without classical treatment, including pre-fractionation, is exposed to hydrogenation processing under hydrogen pressure of 4–7 MPa with the application of nanoheterogeneous catalysts and hydrogen donors, and the generated distillate products undergo hydrofining in a single processing chain.

It is noted that along with the application of hydrofining of coal and petroleum derived raw materials, ozonization is one of the possible ways to increase the yield and improve the quality of products. In [3–5] it is shown the possibility to increase the yields of distillate fractions during ozone treatment of native oils and natural bitumens, as well as products of brown coal liquefaction. In [6] the results of the oxidative modification of coal tar with the ozone-oxygen mixture in benzene, chloroform and without the use of solvents are given.

During ozonization of CT the conversion of its component composition with increasing yield of oxygen-containing fractions - phenol-acid and asphaltene - was achieved. In neutral oils the content of bi- and tricyclic aromatic hydrocarbons - naphthalene and phenanthrene derivatives - increased, the content of toxic heterocyclic and carcinogenic polycyclic arenes decreased significantly, which helped to improve the quality of products produced from coal tar. The chemical composition of CT varies widely enough and depends on the grade composition of coal and the technological mode of coke ovens. The total number of the extracted and accurately identified compounds of sour, basic and neutral nature is more than 300. At the same time the majority of compounds are contained in coal tar in amounts<1% [7]. The main components of coal tar are aromatic, heterocyclic, as well as sulfur, oxygen and nitrogen-containing hydrocarbons. Paraffin, cycloalkan and alkylaromatic compounds are contained in small quantities. The most valuable are individual phenols, cresoles, benzene, naphthalene, toluene, anthracene, pyridine bases, and coal tar pitch - group derived after distillation of oil fractions [8]. The data on definition of component composition of group fractions of coal tar of Altai Koks JSC (Zarinsk city) by the methods of group

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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/cm3; 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/cm3; viscosity 969 mm2/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 dibenzfuran, were identified in its composition. The pattern of distribution of S-, N-, O heteroatoms as a part of aromatic structures of Shubarkul 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). Ozonization 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 ozonization 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 dm3 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 sulphidinge 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 dispergating 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 mcL. 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

Table 2
Characteristics of distillate fractions with boiling point up to 180 °C, obtained from the hydrotreated coal tar (5.0 MPa, 400 °C, τ = 15 min, ozone feeding rate 0.25 ml/min, coal tar: oil paste-forming agent = 1:1, laboratory unit).

Indicator	Catalyst	
	0,025% Mo + 0,03% S	0,05% Mo without adding S
Ozonation time 0 min		
Density at 20 °C, g/cm3	0,7913	0,7533
Content, %:		
Aromatic hydrocarbons	22,9	37,6
Sulphur	0,02	0,07
Iodine number, containment g J_2 /100 g fuel	38,4	42,7
Ozonation time 30 min		
Density at 20 °C, g/cm3	0,7443	0,7531
Content, %:		
Aromatic hydrocarbons	17,2	23,4
Sulphur	0,003	0,006
Iodine number, containment g J_2 /100 g fuel	24,9	30,2
Ozonation time 60 min		
Density at 20 °C, g/cm3	0,7439	0,7475
Content, %:		
Aromatic hydrocarbons	12,8	19,8
Sulphur	0,001	0,004
Iodine number, containment g J_2 /100 g fuel	23,6	30,3
Ozonation time 90 min		
Density at 20 °C, g/cm3	0,7430	0,7226
Content, %:		
Aromatic hydrocarbons	13,9	29,1
Sulphur	0,002	0,002
Iodine number, containment g J_2 /100 g fuel	24,4	35,2

provided with consideration of volumes of each fraction. The hydrocarbon-type content of the received distillate fractions of the coal tar was determined on the Khromatek chromatograph (Germany), the sulfur content - by the POST LEKI P1437 device (Germany) using the method of energy-dispersive X-ray fluorescence spectrometry.

2. Findings and discussion

The results of hydrofining of the ozonized coal tar are given in Table 1, which shows that ozonolysis at the ozonation time of 30 min and at the change of hydrofining temperature of from 350 to 450 °C contributes to the increase of formation of light and medium distillates compared to the process under comparable conditions, but without ozonation. The maximum total yield of these distillates (48.2%) was observed at the ozonation time of the coal tar during 60 min and at the temperature of 400 °C, which is probably due to the deepening of the cracking process, as evidenced by the higher formation of gasoline and diesel fractions (14.8% and 33.4%, respectively) compared to the time of ozone exposure to the coal tar during 30 and 90 min at the same temperature. It should be noted that when the resin hydrofining temperature is varied in the range of 350–450 ° C and the ozonation time is from 30, 60 to 90 min, the total yield of distillate fractions and the yield of distillate fractions from so on. up to 180° C and 180–320° C separately have a maximum at a temperature of 400° C. It appears that at 350 °C the reaction of decomposition of coal tar macromolecules to radicals with lower molecular weight slow down, and at higher temperature (450 °C) the reactions of recombination of radicals occur, resulting in the compaction the coal tar products.

It should be noted that ozonation of the coal tar during 60 min makes it possible to remove sulfur from the coal tar by 95% during the subsequent hydrogenation processing and to produce low-sulfur gasoline fractions with sulfur content of 0.001% (Table 2) and with arena content up to 55% (Table 3). At that, polycyclic arenas, unsaturated compounds and alkyl substituents of aromatic structures with the formation of monocyclic arenas and new compounds with cycloalkyl hydrocarbon framework mainly enter into reaction with ozone.

Table 3
Hydrocarbon-type content of hydrotreated gasoline fractions with boiling point up to 180 °C (5.0 MPa, 400 °C, τ = 15 min, ozone feeding rate 0.25 ml/min, coal tar: oil paste-forming agent = 1:1, laboratory unit).

Hydrocarbons	The implementation of the process of the hydrofining of coal tar	
	Without ozonation	Ozonation time 60 min
Parafins	56,40	25,65
Iso-Paraffins	10,14	11,41
Aromatics	17,20	55,10
Naphthenes	1,40	6,27
Olefins	2,30	1,57

It can be seen from the Table 4 that during hydrofining of the coal tar after ozone exposure the content of aromatic hydrocarbons of the fraction with boiling point to 180 °C increased from 17.2 to 55.1%, iso- paraffin + naphthenetic - from 11.54 to 17.68%, and the content of olefins decreased from 2.3 to 1.57%, which shows the efficiency of the pretreatment of coal tar with ozone. In addition, the hydrofining of the ozonated coal tar in the presence of nanoheterogeneous molybdenum disulfide changes the chemical and hydrocarbon-type content, as well as the yield of light distillate CT fractions.

3. Conclusion

As a result of ozonization and hydrofining of the semi-coking coal tar from the Shubarkol Deposit in the presence of nanoheterogeneous molybdenum sulfide catalyst, the yield of distillate fractions with a boiling point up to 180 °C and the yield of total light distillates increases significantly in comparison with the process without ozonization. The conversion of the hydrocarbon-type content of the fractions with boiling point up to 180 °C is achieved with increasing the yield of aromatic hydrocarbons and reducing sulfur and unsaturated compounds. Introduction of hydrogenation

processes of CT processing and technologies of the coal tar treatment with ozone in coke chemistry will make it possible to increase the degree of beneficial use of native raw hydrocarbons and to improve the quality of the produced distillates and individual chemicals.

CRediT authorship contribution statement

Zh.K. Kairbekov: Supervision. **N.T. Smagulova:** Conceptualization, Methodology. **A.S. Maloletnev:** Investigation, Data curation. **N.A. Abik:** Writing - review & editing. **Y.B. Otynshiyev:** Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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