

UDC 665.7.032.57 : 665.775

DOI: 10.15372/KhUR20170106

Composition of Oils Cracking Products in High-Sulphur Natural Bitumen under Various Conditions

E. B. KRIVTSOV, N. N. SVIRIDENKO, and A. K. GOLOVKO

*Institute of Petroleum Chemistry, Siberian Branch, Russian Academy of Sciences, Tomsk, Russia**E-mail: john@ipc.tsc.ru*

Abstract

The composition of sulphur compounds of oils in high-sulfur natural bitumen of the Ashalchi field (Russia), as well as its thermal cracking products was studied under various conditions. It was demonstrated that depending on thermal treatment conditions gas and coke formation, the composition of the liquid cracking products and sulphur content in them significantly changed. Cracking of bitumen in a reactor autoclave leads to an insignificant decrease in the content of benzothiophene homologs in the composition of oils, the products are enriched with DBT derivatives. Cracking of bitumen in a flow reactor allows decreasing the content of BT homologs by 37 %, and DBT homologs – by 72 rel. % in liquid cracking products.

Key words: natural bitumen, cracking, resins, asphaltenes, sulphur compounds

INTRODUCTION

With the further depletion of reserves of light and medium oils, heavy high-viscosity oils and natural bitumens become an important raw source to satisfy growing needs in fuel. World resources of heavy oils and natural bitumens significantly exceed reserves of light ones and are assessed as more than 810 billion t. Canada and Venezuela have the largest reserves, Mexico, the USA, Russia, Kuwait and China also have significant reserves [1]. Increasing the depth of oil refining with a significant increase in the yield of commercial oil products that are high-quality fuels and chemicals for petrochemical synthesis is the most relevant area for improvement of technologies of oil refining.

At this point, despite a great number of technologies and variants of conversion of heavy petroleum residues (HPR) and natural bitumens, their extraction, transportation, processing and bringing to the merchantability are not cost-effective due to high capital outlays, the cost of hydrogen and quick poisoning (tar-

ring and coking) of the active catalyst surface. Heavy oils and natural bitumens are characterized by high contents of aromatic hydrocarbons, resinous asphalt substances, high concentrations of metals and sulphur compounds, elevated coking capacity. High indicators of density and viscosity significantly increase their extraction self-cost, make virtually impossible transport by existing pipelines [2–6]. Economically justified extraction and processing of heavy high-viscosity oils and natural bitumens appear possible only because of new effective technologies [7–12]. Therefore the knowledge of the composition, structure and properties of sulphur-containing compounds of natural bitumen is of essential practical importance, since allows moving to the study of regularities of their distribution, elaborating more sophisticated techniques of extraction of individual groups of sulphur compounds for the practical use [13–15].

The goal of this work is determining major transformation directions of high molecular mass components and sulphur-containing compounds (SC) of oils in bitumen of the Ashalchi

field in the thermal cracking process under various conditions.

EXPERIMENTAL

Research object

A research object that is natural bitumen on Ashalchi field (Russia, the Republic of Tatarstan) is characterized by high content of sulphur (4.74 %), nitrogen (1.00 %), as well as high molecular mass components – (32.4 mass %, out of them resin – 26.2, asphaltenes – 6.2 mass %; mass fractions of oils is 67.7 %; there is 3.7 mass % of sulphur in oils). The H/C ratio (hydrogen deficiency) in the research object is only 1.52 (this indicator for oils is on average 1.7–1.9). The IBP of bitumen is 109 °C. The total content of distillate fractions boiling out up to 360 °C does not exceed 33 % (with IBP up to 200 °C – 4.6 mass %, 200–360 °C – 27.9 mass %).

Thermal cracking of bitumen

Cracking of bitumen under stationary conditions was conducted in an autoclave with a volume of 12 cm³. The mass of bitumen loadable in the reactor was 7 g. Cracking was carried out at a temperature of 450 °C, the time length was 60, 100 and 120 min. When conducting experiments the mass of the reactor without a sample and the reactor mass with a sample prepared for cracking. After conducting thermal treatment of natural bitumen, the yield of gaseous products was determined according to the loss of the reactor mass with a sample after removing the gaseous products from the reactor. After isolating the products, the reactor was rinsed with chloroform and weighted. After separation of the products, the reactor was washed with chloroform and weighted. The resulting difference between the reactor mass before and after the experiment was determined as solid products (coke).

Cracking of bitumen in a flow mode was conducted in a catalytic setup to study processes under conditions of elevated pressures (Katakton JCS, Novosibirsk, Russia) in nitrogen medium at a temperature of 450 °C and pressure of 20, 40 and 60 atm (gas flow rate was 10

cm³/h). The flow reactor ($d = 15.0$ mm) was filled with quartz chips ($d = 0.5$ – 1.0 mm), the volume of the loaded chips was 10 cm³ to decrease the operating reactor volume and increase the surface of cracking. The raw was supplied to the reactor using a Gilson-305 liquid dosing pump; the raw material feed rate was 0.5 and 1.0 h⁻¹. The liquid cracking products were collected in a high pressure separator. The gaseous products were collected during cracking.

Fractional composition determination

Fractional composition determination of the liquid products of bitumen thermal destruction was assessed according to thermogravimetric analysis data. The thermogravimetric analysis was carried out in air medium using a MOM Q-1000 derivatograph (Hungary) that allow registering the mass loss of the analysis sample with increasing a temperature up to 1000 °C with a heating rate of 10 °C/min.

Material composition determination

Material composition of the initial bitumen and cracking products was determined according to the traditional scheme: first, the asphaltenes content in a sample was determined by “cold” Golde method. For this purpose, the analyte was applied to activated silica gel ASK, into a Soxhlet extractor and hydrocarbon components (oils) were sequentially washed out with *n*-hexane and resins – an ethanol–benzene mixture, 1 : 1.

Sulphur content determination

Sulphur content determination in research samples was carried out using a Spectroscan S energy dispersive X-ray fluorescence analyser (State Standard GOST P 51947–2002) of sulphur in oils and oil products. The measurement range of the mass portion of sulphur is from 0.002 to 5 %.

Group composition of sulphur compounds of oils determination

Gas liquid chromatography (GLC) was carried out using the Crystal-2000M chromato-

graph with the quartz capillary column of $25\text{ m} \times 0.22\text{ mm}$, the stationary phase is SE-54 with helium carrier gas. A flame photometric detector (FPD) was used to analyse sulphur compounds, linear temperature rise was from 50 to 290 °C, column heating rate was 4 °C/min. The qualitative composition of sulphur compounds was determined by comparing the retention times of individual compounds (di-*n*-hexyl sulphide, benzothiophene, and dibenzothiophene) and analytes, as well as using the literature data.

RESULTS AND DISCUSSION

The composition of the initial bitumen and liquid products of thermocracking was studied under various conditions. It was found that the increase in the time length of cracking of bitumen in an autoclave reactor led to destruction of predominantly resinous components. At thermal influence on bitumen of the Ashalchi field during 60 min, the formation of gas (0.4 %) and coke (1.1 mass %) occurs. The yield of oils and asphaltenes increases by 2.8 and 1.2 %, and the content of resins decreases by 5.5 mass % (Table 1). Heat treatment of bitumen during 100 min leads to deeper destruction of resinous components, the total yield of gas and coke increases almost twice. The increase in the time

length of the process up to 120 min leads to deep destruction of resins with the formation of significant amounts of gas and coke. Cracking during 100 min turned out optimum – the increase in the content of oily components was 2.6 % at the total yield of gas and coke of 2.8 %, herewith, destruction of high molecular mass components was 21 rel. %.

Cracking of the initial bitumen at a temperature of 450 °C and time length of 60 min leads to the number increase of fractions IBP-200 °C and 200–360 mass % by 3.1 mass % each, which testifies occurring destructive processes in the reaction medium. The further increase in the time length of cracking does not lead to the increase of the yield of distillate fractions, herewith, the initial boiling point of the liquid cracking products insignificantly decreases.

The composition of the cracking products of bitumen in a flow setup significantly differs from the cracking products in the autoclave reactor. It was found that the pressure decrease (from 60 to 20 atm, raw material feed rate is 1.0 h^{-1}) led to a significant increase in the yield of low molecular mass destruction products of resinous-asphaltenic components (distillate fractions and gas), the content of coke in the products falls. The maximum content of oils was noted at a pressure of 40 atm, the further decrease in pressure to 20 atm to de-

TABLE 1

Composition of the cracking products of bitumen under various conditions

Cracking conditions	IBP, °C	Fractional composition, mass %			Composition of the products, mass %					
		IBP, °C			Gas	Oils	Resins	Asphaltenes	Coke	
		<200	200–360	>360						
Initial bitumen	109	4.6	27.9	67.5	0.0	67.6	26.2	6.2	0.0	
Autoclave reactor										
60 min	113	7.7	31.0	59.8	0.4	70.4	20.7	7.4	1.1	
100 min	106	7.7	30.1	59.4	1.0	70.2	19.7	7.3	1.8	
120 min	103	8.3	29.6	56.1	2.6	68.9	18.0	7.1	3.4	
Flow reactor										
60 atm, 1 h^{-1}	98	18.1	32.7	47.3	0.3	73.5	14.5	6.5	5.2	
40 atm, 1 h^{-1}	84	20.1	29.9	40.9	4.1	75.8	9.9	5.2	5.0	
20 atm, 1 h^{-1}	75	21.6	26.3	38.4	9.2	69.9	9.2	5.9	4.7	
60 atm, 0.5 h^{-1}	69	26.0	28.4	27.7	11.5	62.1	10.9	5.4	10.1	
40 atm, 0.5 h^{-1}	61	29.2	25.7	20.7	12.8	66.9	9.6	1.8	8.9	
20 atm, 0.5 h^{-1}	45	43.1	18.3	15.8	19.2	69.9	4.3	3.0	3.6	

struction of 5.9 % of oils with the formation of additional amounts of gaseous and coke-like cracking products. In comparison with the composition of the initial bitumen, the content of oils and liquid cracking products is increased, that of resinous-asphaltenic components is reduced by more than 35 % at a pressure of 60 atm and above 50 rel. % at pressures up to 20–40 atm.

Cracking of bitumen in a flow reactor (20–60 atm, the raw material feed rate is 1.0 h^{-1}) allows significantly decreasing the initial boiling point of liquid cracking products (by $34 \text{ }^\circ\text{C}$). It was found that the maximum increase of the yield of distillate fractions (IBP– $360 \text{ }^\circ\text{C}$) occurs at a pressure of 60 atm – 18.3 mass %. A decrease in pressure in the reactor to 40 atm leads to an additional increment of low-boiling fractions by 17.5 mass %. The increase of gasoline fractions of 17.0 % and reduction of diesel fractions (by 1.6 mass %) are observed at a pressure of 20 atm as destructive consequences of a part of oils with the formation of additional amounts of gas.

A decrease in the raw material feed rate up to 0.5 h^{-1} leads to an increase in stay of raw materials in the reactor (heat treatment time length) and therefore significantly increases cracking level of all initial bitumen components. A decrease in pressure from 60 to 40 atm leads to an increase in the formation of gas (from 11.5 to 12.8 %) and oils (from 62.9 to 66.9 %), deep destruction of resins (the residual content is 9.6 mass %), as well as to a decrease in the amount of asphaltenes and coke in the

products. A decrease in pressure to 20 atm leads to a change in the directionality of destruction reactions of high molecular mass bitumen components to the side of the formation of significant amounts of low molecular mass components that are gas (19.2 %) and gasoline fraction (43.1 mass %). The content of resins and asphaltenes is decreased by 84 and 52 rel. %, that of oils is increased by 2.3 mass %.

At the raw material feed rate of 0.5 h^{-1} and pressure of 60 atm, an increase in the content of IBP–200 and 200– $360 \text{ }^\circ\text{C}$ fractions is observed in the composition of liquid cracking products by 21.4 and 0.5 mass %, respectively (in comparison with the initial bitumen). Reduction in pressure to 40 atm leads to the decrease in IBP of the products by $48 \text{ }^\circ\text{C}$ and an increase in the number of gasoline fractions (by 24.6 %), the content of diesel fractions reduces by 2.2 mass %. The initial boiling point of liquid cracking products at 20 atm is only $45 \text{ }^\circ\text{C}$, the maximum yield of IBP– $200 \text{ }^\circ\text{C}$ fractions (43.1 mass %) driven by deep cracking of resinous-asphaltenic components and kerosene-gasoil fractions of bitumen is observed. Thus, the increase in the raw material feed rate and pressure slows down cracking reactions of high molecular mass bitumen components with the formation of distillate fractions.

The composition of sulphur compounds (SC) in the initial bitumen oils is presented in Fig. 1. Substituted benzothiophenes (BT) prevail in the Ashalchi bitumen field. With an increase in the degree of substitution, the content of BT homologs

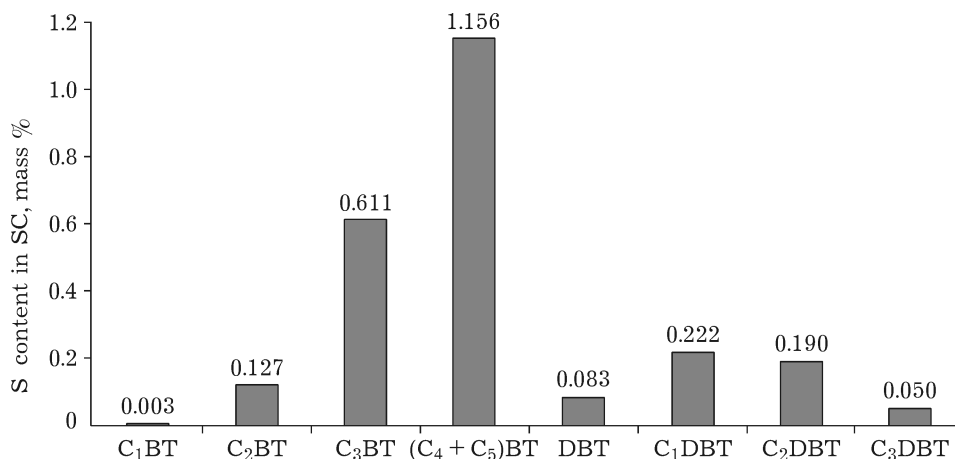


Fig. 1. Group composition of sulphur compounds (SC) in bituminous oil from the Ashalchi natural bitumen field.

increases, and dibenzothiophenes (DBT) decreases. The content of sulphide sulphur (determined according to the difference) is 1.26 mass %.

Based on chromatography data on the content of benzo- and dibenzothiophene (BT and DBT) homologs in the initial bitumen and cracking products, the calculation of the SC content (S total, S in oils, Σ BT, Σ DBT) of isolated oils was carried out (Table 2). The Ashalchi bitumen field contains 78 % from the total amount of sulphur, including sulphide sulphur – 1.26 mass %. It was found that cracking of natural bitumen in an autoclave reactor led to a decrease in sulphur content in liquid cracking products and oils (by 14 rel. %). An increase in the time length of heat cracking of bitumen from 60 to 120 min contributes to an insignificant increase in desulphurization of liquid cracking products. The content of BT homologs almost does not change, DTB homologs decreases but exceed such in the initial bitumen. Apparently, molecules of resins of this bitumen contain sulphur atoms mainly in the composition of dibenzothiophene structures that fall into oils at cracking. A decrease in the content of DBT homologs at an increase in the time length of thermal cracking of bitumen is probably driven by their participation in occurring condensation reactions following the route: resins \rightarrow asphaltenes \rightarrow coke.

Cracking of bitumen in a flow reactor allows significantly increasing the degree of des-

ulphurization of liquid products (up to 49 %), oils – to 44 %, the content of sulphide sulphur in oils significantly reduces. The composition of organosulphur compounds (OSC) of oils in the products of cracking of bitumen in a flow setup significantly differs from cracking products in an autoclave reactor. It was found that a decrease in pressure (from 60 to 20 atm, the raw material feed rate is 1.0 h⁻¹) led to a decrease in sulphur content in liquid products and oils, the amount of sulphide sulphur is less than half from the original value. The removal degree of BT homologs does not exceed 31 rel. %, DBT homologs – 8 rel. %. This is probably explained by occurring destruction reactions of resins and asphaltenes molecules with a transition of low molecular mass sulphur-containing fragments (newly formed BT and DBT homologs) into the composition of oils.

A decrease in the raw material feed rate leads to an increase in the destruction depth of raw material components and consequently, to a significant increase in the destruction degree of all SC groups. A decrease in pressure (from 60 to 20 atm, the raw material feed rate is 0.5 h⁻¹) allows additionally removing 0.7 % sulphur from the composition of the products, the sulphur content in oils decreases by 0.82 %, including sulphide – by 0.36 mass %. Significant destruction of BT homologs (37 %) and DBT – 72 % of the initial quantity, occurs. Taking into account a high yield of gas-

TABLE 2

Content of sulphur compound in the cracking products of bitumen under various conditions

Cracking conditions	Content, mass %				
	S _{tot}	S in oils	S _{sulph}	Σ BT	Σ DBT
Initial bitumen	4.74	3.70	1.26	10.92	3.46
Autoclave reactor					
60 min	4.06	3.17	0.81	8.81	5.04
100 min	4.00	3.12	0.90	8.56	4.35
120 min	3.98	3.12	0.94	8.81	3.78
Flow reactor					
60 atm, 1 h ⁻¹	3.21	2.74	0.64	8.50	3.95
40 atm, 1 h ⁻¹	3.08	2.56	0.62	7.08	4.25
20 atm, 1 h ⁻¹	2.99	2.48	0.60	7.57	3.17
60 atm, 0.5 h ⁻¹	3.11	2.88	0.64	9.73	2.82
40 atm, 0.5 h ⁻¹	2.90	2.41	0.51	8.48	3.59
20 atm, 0.5 h ⁻¹	2.41	2.06	0.28	6.91	0.96

eous cracking products one can suggest that the major amount of sulphur is removed from raw material composition as hydrogen sulphide.

CONCLUSION

It was found that bitumen on the Ashalchi field in an autoclave reactor led to insignificant destruction of resins and asphaltenes. The withdrawal of cracking products from the reaction zone allows increasing destruction of resinous components (to 63.0 rel. %), due to which the yield of IBP-360 °C fractions increases by 28.9 mass % and the sulphur content in cracking products reduces by 51 rel. %.

Cracking of bitumen in an autoclave reactor leads to a minor reduction in the content of benzothiophene homologs in the composition of oils. Products are enriched with DBT derivatives. Apparently, molecules of resins of this bitumen contain sulphur atoms mainly in the composition of dibenzothiophene structures.

Cracking of bitumen in a flow reactor allows decreasing the content of BT homologs by 37 % and DBT homologs – by 72 rel. %. The content of DBT homologs decreases probably due to occurring condensation reactions following the route: resins → asphaltenes → coke.

REFERENCES

- 1 Okunev A. G., Parkhomchuk E. V., Lysikov A. I., Parunin P. D., Semeikina V. S., Parmon V. N., *Russ. Chem. Rev.*, 9 (2015) 987.
- 2 Haohua Gao, Gang Wang, Rong Li, Chunming Xu, and Jinsen Gao, *Energy Fuels*, 3 (2012) 1880.
- 3 Liu M., Wang M., Zhang L., *Energy and Fuels*, 29, 2 (2015) 702.
- 4 Shahandeh H., Li Z., *Energy and Fuels*, 30 (2016) 5202.
- 5 Jinhong Zhang, Honghong Shan, Xiaobo Chen, Chunyi Li, Chaohe Yang, *Ind. Eng. Chem. Res.*, 2 (2013) 658.
- 6 Zhang J.X., Zhou Y., Xu Y., Tian H.P., *China Petrol. Proc. Petrochem. Techn.*, 16 (2014) 7.
- 7 Sviridenko N. N., Krivtsov E. B., Golovko A. K., *Chem. Technol. Fuels Oils*, 52, 3 (2016) 285.
- 8 Du H., Liu D., Li M., Wu P., Yang Y., *Energy and Fuels*, 29, 2 (2015) 626.
- 9 Guo A., Zhou Y., Chen K., Xue Z., Wang Z., Song H., *J. Anal. Appl. Pyrol.*, (2014) 115.
- 10 Sviridenko N. N., Krivtsov E. B., Golovko A. K., *Fundam. Res.*, 8(4), (2014) 854.
- 11 Ongarbayev Y. K., Golovko A. K., Krivtsov E. B., Imanbayev Y. I., Tileuberdi E., Tuleutaev B., Mansurov Z. A., *Solid Fuel Chem.*, 50, 2 (2016) 81.
- 12 Nassar N. N., Hassan A., Pereira-Almao P., *Energy Fuels*, 25 (2011) 1566.
- 13 Sviridenko N. N., Golovko A. K., Dombrovskaya A. S., Krivtsova N. I., *Procedia Chem.*, 10 (2014) 326.
- 14 Trejo Fernando, Ancheyta Jorge, Rana Mohan S., *Energy Fuels*, 23 (2009) 429.
- 15 Hauser A., Humaidan F., Al-Rabiah H., Halabi M. A., *Energy Fuels*, 28 (2014) 4321.