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Effect of Radical-Forming Additives on the Composition of Initiated Cracking Products of Bitumen from the Bayan-Erkhet Deposit

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Abstract

The paper deals with the research on the composition of cracking products of the bitumen from the Bayan-Erkhet deposit (Mongolia) upon varying process times, temperatures, and also in the presence of radical-forming additives (styrene, benzoyl peroxide, and di-*tert*-butyl peroxide). Typical features of changing the material and fractional composition of cracking products were demonstrated depending on conditions. The transformation nature of resinous-asphaltenic components was explored.

Key words: natural bitumen, cracking, resins, asphaltenes, radical-forming additives

INTRODUCTION

Lately, research related to making new highly efficient technologies for the processing of heavy hydrocarbon feedstock (HHF) has been extensively carried out. The latter includes heavy and extra-heavy crude oil, natural bitumen and bitumen-saturated rocks, asphaltite, *etc.* [1–3]. This is due to a steady reduction in the fraction of recovered light oil and an annual increase in the quantity of heavy oil involved in processing [4, 5]. Earlier, such a feedstock has been almost unused in the petrochemical industry. The development of processing methods for heavy oil residues and natural bitumen is considered to be a promising area. Factual processing methods of HHF processing are expensive and do not allow reaching the high-level conversion of natural bitumen components into commercial oil products (gasolines, diesel fuel, *etc.*).

A great deal of research is linked to exploring techniques that might ensure the deriving lighter, so-called synthetic crude oil (SO), based on the heavy feedstock. The former may be further processed according to the existing schemes without significant changes in technological processes at

oil refinery [6–9]. One of the promising method for producing SO is initiated cracking of HHF in the presence of organic compounds (peroxides, *etc.* [10–12]). The latter are able to generate free radicals directly inside the reaction system at low temperatures. Owing to the radical formation, the progression of radical-chain cracking reactions of hydrocarbons and resinous-asphaltenic components starts to work. A distinctive feature of cracking in the presence of radical-forming additives (RFA) consists in the intense formation of radicals already at the step of feedstock heating, which substantially facilitates process initiation, has an effect on the direction of proceeding reactions and, accordingly, on the composition of HHF cracking products. Hence, there is an opportunity to use various groups of organic compounds acting as RFA to obtain SO with a low content of high-molecular weight and heteroatomic compounds and high levels of low-boiling fractions. In other words, the latter are likely to produce products with the optimum chemical composition.

The objective of this research was to determine the effect of RFA (benzoyl peroxide, di-*tert*-butyl peroxide, and styrene) on the process of

initiated cracking of components of highly resinous natural bitumen.

EXPERIMENTAL

Research object

A sample of the bitumen from the Bayan-Erkhet deposit (Mongolia) was selected as the research object (Table 1). Bituminous rocks of this deposit are notable for a large content of organic matter (17–19 mass %). This bitumen is characterised by a high content of resinous-asphaltenic compounds (almost 55 %, including resins of over 52 mass %); atomic H/C ratio reaches 1.85. A relatively low content of heteroatoms is worth noting. In total, their content is not higher than 2 mass %. The level of distillate fractions is 15 mass % and there is almost no gasoline fraction (1.4 mass %). As a result, the initial boiling point (IBP) of bitumen is higher than 170 °C.

Thermal cracking of bitumen

Cracking under stationary conditions was performed in an autoclave with a capacity of 12 cm³ at 350, 400, and 450 °C; a time period of 30–120 min. The mass of bitumen loaded into the autoclave was 7 g. Prior to cracking, the reactor mass without the sample and with it was recorded. Gaseous products were removed after the thermal treatment of natural bitumen followed by determining their yields according to reactor mass loss. Afterwards, reactor was rinsed with chloroform and weighted. The masses of solid reaction products formed were determined as differences of reactor masses before and after the experiment.

In order to increase the degree of decomposition of resinous-asphaltenic components, the thermal cracking of bitumen was carried out in presence of RFA. Sigma-Aldrich chemicals were used as such. They included benzoyl peroxide (PB) (CAS number 94-36-0, a concentration of 76.0 mass %, water as a stabilizer), di-*tert*-butyl peroxide (DTBP) (CAS number 110-05-4, a content of 99.4 mass %, H₂O as a stabilizing agent). The chemical agents are unstable at temperatures above 106 and 110 °C, respectively. In addition, styrene (CAS number 100-42-5, a concentration of 99.9 mass %, 4-*tert*-butylcatechol as a stabilizer) was employed. The agent is able to generate radicals at temperatures above 350 °C [12]. The quantity of additives varied between 1 and 5 mass % of bitumen mass.

TABLE 1
Characteristics of the bitumen from the Bayan-Erkhet deposit

Indicators	Value
Average molecular mass, Da	578
Material composition, mass %:	
oils	45.2
resins	52.5
asphaltenes	2.3
Content, mass %:	
sulphur	0.45
carbon	85.26
hydrogen	13.13
nitrogen	0.98
oxygen	0.18
H/C atomic ratio	1.85
Fractional composition, mass % at <i>t</i> , °C:	
IBP	172.1
IBP-200	1.4
IBP-200-260	13.6
IBP > 360	85.0

Fractional composition determination

The fractional composition of liquid products from thermal decomposition of bitumen was determined by thermogravimetric analysis. The measurements were carried out in the air using the Q-1000 derivatograph manufactured by MOM company (Hungary), which allowed recording the mass loss of the analytical sample with an increase in temperature to 1000 °C at a heating rate of 10 °C/min

Determining material composition

The material composition of the initial bitumen and cracking products was determined according to the common technique. Asphaltenes content in the sample was determined by the “cold” Golde method. Afterwards, resin content in the resulting maltenes was determined by the adsorption method: the analysed product was applied onto ASK silica gel, placed into a Soxhlet extractor, and sequentially extracted hydrocarbon components (oils) with *n*-hexane, whereas resins – with a 1 : 1 ethanol/benzene mixture.

Structural group analysis of resins and asphaltenes

Resins and asphaltenes isolated from the initial and thermolysed bitumen species were explored by structural group analysis (SGA) according to the technique developed at the Institute of Petroleum Chemistry of the Siberian Branch of the Russian Academy of Sciences (IPC SB RAS) [13].

The method is premised on the combined use of determination results for the elemental composition, the average molecular mass and ^1H NMR-spectroscopy data and allows computing the average distribution of atoms between structural group of molecules of high-molecular-mass compounds in natural bitumen. This distribution provides information regarding the molecular size and structure, and also the number of various structural groups.

The elemental analysis of resins and asphaltenes of the initial bitumen and cracking products was performed with Vario El Cube CHNS elemental analyser. The molecular masses of compounds were determined by cryoscopy in naphthalene using a Krion instrument (IPC SB RAS, Tomsk). The ^1H NMR spectra were recorded on NMR Fourier spectrometer Bruker AVANCE-300 using CDCl_3 and HMDS as a solvent and internal standard, respectively, at a 1 % concentration of resins and asphaltenes.

Chromatographic analysis of gases

Gaseous hydrocarbons formed upon bitumen cracking were analysed by gas chromatography on a Crystal-5000 GC, according to GOST 31371.3-2008. Hydrogen, oxygen, and nitrogen were determined using a NaX sieves column (80-100 mesh fraction, a column length of 1 m, and an inner diameter of 2 mm), the carrier gas (argon) flow rate of $30\text{ cm}^3/\text{min}$. A column filled with HayeSep K polymer adsorbent (the 80-100 mesh fraction, a column length of 3 m, an inner diameter of 2 mm) was used for partitioning of $\text{C}_1\text{-C}_6$ hydrocarbons, a helium carrier gas flow of $30\text{ cm}^3/\text{min}$. The analysis was carried out in the temperature programming mode using two columns in parallel between 35 and $170\text{ }^\circ\text{C}$, a heating rate of $5\text{ }^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

In order to determine the thermal stability of components of the natural bitumen from the Bayan-Erkhet deposit (Mongolia), cracking was carried out at 350, 400, and $450\text{ }^\circ\text{C}$. Process time was 30, 60, 90, and 120 min (Table 2).

As determined, the condensation of oil components to form resins at cracking temperatures of $350\text{-}400\text{ }^\circ\text{C}$ proceeds faster than the compaction of resins *via* the resins \rightarrow asphaltenes \rightarrow coke path. Formation processes of gas and coke proceed insignificantly; the IBP of liquid cracking products (the total amount of oils, resins and asphaltenes) is increased and the fractional composition is worsened compared to the initial bitumen.

Increasing cracking temperature till $450\text{ }^\circ\text{C}$ results in changing proceeding reactions equilibrium. For example, cracking reactions of resins to form additional quantities of oils and asphaltenes are significantly accelerated and the IBP of liquid cracking products is reduced by more than $50\text{ }^\circ\text{C}$. Increasing cracking time between 30 and 120 min at this temperature leads to a reduction in the yield of liquid products due to the development of gas and coke formation processes. A significant reduction in the quantity of resins in the composition of cracking products is worth noting. It is known that there is a trend for resins in natural bitumen to form unstable intermediates that are capable of further compaction to form asphaltenes [14]. Oils in maximum quantities (about 44 mass %), and also components of distillate fractions, are generated at a cracking time of 120 min but the quantity of by-products (gas and coke) reach almost a half of the mass of the initial bitumen.

Relying on the data acquired (fractional composition, decomposition depth of oils, and material balance of cracking products), the optimum conditions for further experiments on the ther-

TABLE 2
Composition of bitumen cracking products under various conditions

Cracking conditions	$T_{\text{IBP}},\text{ }^\circ\text{C}$	Fractional composition at $T, \text{ }^\circ\text{C}$ (mass %)			Product composition, mass %				
		<200	~200-360	>360	Gas	Oil	Resins	Asphaltenes	Coke
Initial bitumen	172.1	1.4	13.6	85.0	0	45.2	52.5	2.3	0
350 $^\circ\text{C}$, 60 min	240.3	0	6.3	89.6	2.0	32.3	61.2	2.4	2.1
400 $^\circ\text{C}$, 60 min	229.2	0	6.5	89.1	2.4	36.1	56.7	2.8	2.0
450 $^\circ\text{C}$, 30 min	120.3	1.0	4.7	90.4	2.6	37.9	52.1	6.1	1.3
450 $^\circ\text{C}$, 60 min	98.9	1.1	4.8	64.3	9.1	39.0	24.9	13.3	13.7
450 $^\circ\text{C}$, 90 min	97.6	4.0	11.3	55.7	9.6	40.0	23.0	8.0	19.4
450 $^\circ\text{C}$, 120 min	74.5	7.2	10.3	35.9	11.2	44.0	2.9	6.5	35.4

TABLE 3

Composition of bitumen cracking products (450 °C, 60 min) with radical-forming additives (RFA)

Cracking conditions	T_{IBP} , °C	Fractional composition at T , °C (mass %) :			Product composition, mass %				
		<200	200–360	>360	Gas	Oil	Resins	Asphaltenes	Coke
Initial bitumen	172.1	1.4	13.6	85.0	0	45.2	52.5	2.3	0
Bitumen cracking	98.9	1.1	4.8	64.3	9.1	39.0	24.9	13.3	13.7
+ DTBP, 1 %	117.8	1.6	11.9	79.5	1.4	47.4	36.3	8.3	6.6
+ DTBP, 3 %	85.9	4.8	12.6	63.1	5.6	50.1	15.5	19.0	9.8
+ DTBP, 5 %	71.0	8.0	13.7	55.5	8.0	45.0	13.9	17.2	15.9
+ PB, 1 %	137.3	1.0	8.2	74.2	4.7	35.6	39.8	8.0	11.9
+ PB, 3 %	110.6	2.6	7.2	75.7	4.8	44.7	23.4	17.4	9.7
+ PB, 5 %	43.1	20.6	7.1	63.5	4.1	43.4	37.4	10.4	4.7
+ Styrene, 1 %	180.1	0.1	9.0	86.4	3.8	42.5	49.7	3.3	0.7
+ Styrene 3 %	172.0	1.1	12.9	83.7	1.5	45.1	49.4	3.2	0.8
+ Styrene, 5 %	50.3	18.8	15.9	63.3	1.3	49.8	45.2	3.0	0.7

mal treatment of the bitumen from the Bayan-Erkhet deposit in the presence of RFA were selected as follows: a temperature of 450 °C and a process time of 1 h.

As demonstrated by early research, the use of RFA is efficient for HHF processing [15]. It is suggested that at a low temperature, additives are decomposed to form radicals that significantly change directions of radical-chain reactions of cracking of HHF components. This research used HHF to slow down condensation processes of resins into asphaltenes and then to coke, and also to accelerate decomposition reactions of bitumen components.

In order to increase the depth of cracking of oils of the bitumen from the Bayan-Erkhet, the optimum amount of additives was selected. Table 3 lists the material balance, and also the material and fractional composition of liquid products of bitumen cracking in the presence of RFA.

As determined, the addition of DTBP (1 mass %) significantly slows down the cracking reaction of oils (compared to cracking products of bitumen), which leads to a decrease in gas and coke formation, and also to an increased content of oils. Here-with, the fractional composition of liquid cracking products changes insignificantly. An increase in the amount of DTBP to 3 mass % results in initiating deep decomposition processes of resins (the residual content is 26 % of the initial one). Low-molecular-mass fragments of initiated cracking products of resins fall into the composition of oils. Apparently, the naphthenic and alkyl framing of oil molecules [16] is cracked to form oil components; aromatic fragments extensively participate in the condensation reaction to form secondary asphaltenes and coke.

When the amount of the DTBP additive is increased to 5 mass %, all cracking reactions are accelerated. Gases (about 8.0 mass %) and additional distillate fractions are generated based on oil components. Most oil molecules activated with *tert*-butyloxyl radicals are condensed to form many secondary asphaltenes and coke.

The addition of PB in the amount of 1 mass % is favourable to the progression of condensation reactions of bitumen components. The content of oils and resins is decreased compared to the composition of the initial bitumen. The amount of newly formed distillate fractions is low. Asphaltenes and coke are generated in significant amounts (8 and 12 mass %, respectively). An increase in the mass of PB by 3 times primarily initiates reactions with the involvement of resins (the contents of the latter is decreased by 29 mass %). The content of asphaltenes (condensation products of resins) and oils (decomposition products of resins) is increased. The condensation rate of asphaltenes to coke is slowed down. The addition of PB 5 mass % causes significant slowing down the condensation reaction of bitumen components according to the resins → asphaltenes → coke path. Cracking reactions of oils to form components of distillate fractions proceed intensely.

When styrene is used as RFA, a distinguishing feature of the process is a low yield of gaseous cracking products. The latter is reduced when additive concentration is increased. Coke formation is minimum not depending on the mass of styrene. Secondary asphaltenes are almost not formed and their content is decreased when additive concentration is increased. The listed facts indicate that styrene has the maximum ability to

TABLE 4

Composition of gaseous cracking products of bitumen (450 °C, 60 min) with radical-forming additives (RFA)

Gases	Content, mass %			
	Cracking	Cracking + DTBP 5 mass %	Cracking + PB 5 mass %	Cracking + styrene 5 mass %
H ₂	0.38	0.02	0.01	0.01
CH ₄	1.80	1.43	0.42	0.45
C ₂ H ₆	1.32	0.50	0.91	0.30
C ₃ H ₈	2.19	0.37	1.51	0.35
C ₃ H ₆	0.03	0.17	0.26	0.01
<i>iso</i> -C ₄ H ₁₀	Absent	1.29	0.33	0.07
<i>n</i> -C ₄ H ₁₀	1.10	0.02	0.03	0.03
ΣC ₄ H ₈	1.41	3.06	0.14	0.06
<i>iso</i> -C ₅ H ₁₂	0.13	0.40	0.28	0.02
<i>n</i> -C ₅ H ₁₂	Absent	0.11	0.20	Absent
ΣC ₅ H ₁₀	0.61	0.51	Absent	Absent
ΣC ₆ H ₁₄	0.13	0.12	Absent	Absent
ΣGases	9.10	8.00	4.10	1.30

inhibit condensation reactions of bitumen components among the additives listed. Cracking reactions in the presence of styrene are typical for resins (their content is decreased by 7 % compared to the composition of the initial bitumen) to form oils in small amounts (4.6 mass %).

Oil cracking proceeds relatively fast to form many low-molecular-mass components that fall into the composition of distillate fractions.

The research was carried out on cracking products of bitumen in the presence of RFA (see Table 3). The content of distillate fractions in the composition of liquid products of bitumen thermal cracking is reduced at 450 °C as determined. There is a 9 mass % decrease in the content of the fraction (IBP of 360 °C) probably due to the partial cracking of low-molecular-mass components to form gaseous products. Cracking with DTBP additives allows the additional preparation of no more than 6 mass % of fractions with IBP of 360 °C mainly due to the formation of the fraction with IBP of 200 °C. Introducing BP results in changing the balance of occurring condensation and decomposition reactions of bitumen components towards the latter. Asphaltene and coke formation is significantly reduced; oil and resin cracking proceeds to form components of distillate fractions. There is a redistribution of the fractional composition of cracking products. In other words, the content of diesel fractions is reduced (by 1 %) and the yield of gasoline distillates is increased (by 18 mass %); the IBP of liquid cracking products is decreased by 129 °C.

The addition of styrene in the amount of 1–3 mass % does not produce significant changes in the yields of fractions with IBP of 360 °C.

An increase in the amount of the additive to 5 mass % leads to the appearance of significant amounts of light fractions in the liquid products. For example, there is an increase in gasoline (more than by 17 %) and diesel distillates. Considering the minimum formation of gas and coke, and also a minor decrease in the content of resins (by 7 mass % compared to the initial value), one may suggest that high-molecular-mass oil components are mainly exposed to cracking due to reaching the required concentration of radicals in the reaction medium.

The difference in the number of RFA required to produce the maximum amounts of distillate fractions is probably due to the varying structure and life time of radicals obtainable upon the decomposition of the former. The use of initiating additives results in an increased decomposition degree of high-molecular-mass components. It is possible to reduce the content of resins and asphaltenes in thermal cracking products of bitumen from the Bayan-Erkhet deposit due to an increase in the concentration of radicals. Moreover, a decrease in the yield of the resulting coke is often likely.

As demonstrated by analysis of gaseous products, bitumen cracking without additives mainly leads to the formation of C₁–C₄ hydrocarbon gases (Table 4). There are *iso*- and *n*-pentane compounds, and also hexane derivatives in small amounts among the latter; there is no carbon dioxide. When DTBP is added, the major cracking products are isobutane and butenes (about 50 % of the total amount of all gases). They are likely to be the final products of thermal transformations of DTBP. There are also C₁–C₃ hydrocarbons

TABLE 5

Structural-group parameters of resin molecules of bitumen cracking products with RFA

Calculated parameters	Resins				
		Initial	Cracking	Cracking + DTBP 3 mass %	Cracking + PB 5 mass %
Molecular mass, Da		581	616	589	739
Number of atoms in average molecules	C	41.73	44.79	41.70	51.39
	H	65.88	64.66	57.09	79.18
	N	0.46	0.40	0.64	0.43
	S	0.08	0.08	0.06	0.08
	O	0.31	0.33	1.27	2.12
Number of structural blocks	m_a	1.02	1.68	1.60	1.48
Number of various carbon atoms in molecule	C_{ar}	8.53	16.74	15.26	13.15
	C_{napht}	15.72	5.94	11.54	10.92
	C_p	17.48	22.11	14.90	27.31
	C_α	4.18	3.51	6.25	5.14
	C_γ	4.82	3.43	2.67	4.15
Ring composition	K_o	5.54	5.08	6.26	5.63
	K_a	1.80	3.60	3.45	2.96
	K_{sat}	3.74	1.48	2.81	2.67
Degree of substitution of aromatic rings	σ_a	0.55	0.27	0.52	0.49
Aromaticity criterion	f_a	20.43	37.38	36.60	25.60

that are bitumen cracking products. The lack of *n*-butane is worth noting. The composition of gaseous products of thermolysis products bitumen in the presence of BP and styrene is largely similar to that of hydrocracking gases. In both cases, the fraction of C_1 – C_3 hydrocarbon is about 70 % of the total amount of gases there are almost no C_{6+} hydrocarbons. The distribution of C_4 gases is similar.

As demonstrated by structural-group analysis of molecules of resins in bitumen from the Bayan-Erkhet deposit (Table 5), they mainly contain aliphatic fragments and naphthenic rings. The aromaticity criterion is relatively low. It is known that such structures are readily exposed to cyclization and dehydration reactions under thermal impact conditions to form condensed polyaromatic compounds. Herewith, there is breaking off low-molecular-mass fragments that form components of the fraction with an IBP of 360 °C. As the mechanism of cracking reactions is radical, introducing compounds that are able to generate radicals into the reaction medium leads to shifting the equilibrium towards the formation of low-molecular-mass products.

As determined, the molecular mass of resins remains almost unchanged with the optimum amount of DTBP (3 mass %) additives. The aromaticity criterion, and also the number of structural blocks m_a , and their size, are increased. That is explained by the progression of resins →

asphaltenes → coke compaction reactions due to the deep destruction of alkyl fragments (the fraction of alkyl carbon atoms (C_p) is decreased). The average length (C_γ) of alkyl substituents in aromatic moieties is decreased. The number of aromatic rings is increased and the content of naphthenic rings is decreased, which attests to the progression of dehydration reactions that lead to the formation of the more aromatized species.

As demonstrated by structural group analysis of cracking products of bitumen from the Bayan-Erkhet deposit with the addition of PB 5 mass % (the optimum amount), the molecular mass of resins is maximum among all samples analysed. The number of aromatic rings in resin species is increased and that of naphthenic rings is decreased, which is related to processes of the aromatization of the latter. Aromaticity criterion of resins is higher than that in the initial species. The number of structural blocks (m_a) of resin species remained unchanged and their average size was decreased.

CONCLUSION

The Bitumen from the Bayan-Erkhet deposit contains resinous components in prevalent amounts (52.5 mass %). As determined, high-molecular-mass compounds are prevailing at thermal treat-

ment temperatures of 350–400 °C, whereas reverse reactions of decomposition of resins and asphaltenes to form light hydrocarbons are prevalent at 450–500 °C. And what is more, coke formation is increased.

The effect of radical-forming additives (RFA) on thermal transformations of high-molecular-mass compounds has been illustrated. Additives allow an increase in the decomposition degree of resinous components, which results in a decrease in the content of resinous-asphaltenic compounds in cracking products, an increase in the yield of light hydrocarbons, and also to reduced coke formation. The relationship has been found between the transformation degree of components of heavy feedstock *vs* quantities and types of the initiating additive. As demonstrated, the introduction of styrene and PB in the amount of 5 % and DTBP of 3 mass % allows reaching the highest yield of distillate fractions.

Distinguishing structural-group parameters of resin and asphaltene molecules in the initial bitumen have been determined. Average species of resins and asphaltenes almost do not contain heteroatoms. The amount of aromatic and naphthenic compounds is almost the same. There are significant amounts of relatively long alkyl substituents. The addition of DTBP 3 mass % causes a reduction in the number of naphthenic rings and the total amount of cyclic fragments due to the fraction of aromatic rings. The number and the length of aliphatic substituents are significantly decreased. The content of oxygenated compounds and the number of structural blocks of the molecules are increased. The addition of PB 5 mass % followed by cracking leads to the decomposition

of naphthenic fragments and aliphatic chains in part. The number of average structural blocks of the molecules of resins and asphaltenes is increased. Herewith, the size of the components is substantially decreased.

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