Chemistry for Sustainable Development **17** (2009) 169–175

UDC 66.081:547.912

Effect of Mechanical Treatment on the Composition of Bitumen-Saturated Sandstone

G. S. PEVNEVA[1], E. V. IVANOVA[1], V. G. SURKOV[1], A. K. GOLOVKO[1] and A. F. SAFRONOV[2]

[1]*Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences,*
Pr. Akademicheskiy 4, Tomsk 634021 (Russia)

E-mail: pevneva@ipc.tsc.ru

[2]*Institute for Petroleum and Gas Problems, Siberian Branch of the Russian Academy of Sciences,*
Ul. Oktyabrskaya 1, Yakutsk 677891 (Russia)

(Received July 10, 2008; revised November 19, 2008)

Abstract

Changes in the composition of the organic constituent of bitumen-saturated sandstone arising during its mechanical treatment with AGO-2 set-up in the atmosphere of argon and hydrogen were studied. It was demonstrated that mechanical treatment in argon environment causes a decrease in the yield of bitumoid (the organic component), a decrease in the content of pyrobitumen, oil, saturated hydrocarbons, and triarenes, the fraction of gum species increases sharply. During sandstone treatment in the atmosphere of hydrogen, no substantial changes occur in the material constitution of the bitumoid in comparison with the initial sample, but the content of saturated, bi- and triaromatic hydrocarbons in the group composition of this bitumoid is essentially smaller in comparison with the bitumoid of the initial sandstone.

Key words: bitumen-saturated sandstone, mechanical treatment, product composition

INTRODUCTION

Increasing consumption of hydrocarbon raw material, limited amount and irreplaceability of the resources of liquid fuel stimulate investigation of the alternative sources of hydrocarbon raw materials. The resource basis of hydrocarbons (HC) may be broadened due to processing bitumen-saturated rocks (bitumen-saturated sandstone and natural bitumen) the resources of which are very large at the territory of Russia. The technologies of obtaining synthetic oil from the raw material of this kind are most well developed in Canada. At present, there are no economically favourable industrial technologies of profound processing of solid fossil fuel in Russia.

One of the methods of destruction of high-molecular compounds the content of which is the organic part of bitumen-saturated rocks may exceed 50 % is mechanical activation. Results of the investigation of the effect of mechanical treatment (MT) on oil and coal components were presented in [1–12]. The authors of [10] studied changes in the chemical composition of HC, gum, pyrobitumen as a result of MT of black oil. Mechanical treatment of high-molecular HC – the major components of oil residues – leads to the destruction of chemical bonds and the formation of compounds with smaller molecular mass and therefore lower boiling point [1–3]. Mechanical treatment of coal pyrobitumen species causes their destruction and the formation of both relatively low-molecular substances (oil species) and more complicated compounds (pre-pyrobitumen species) [5, 6].

Possible directions of mechanochemical transformations of molecules include such reactions as decomposition, isomerization, cyclization, addition. The formation of compounds both with smaller and with larger molecular mass occurs; isostructural compounds, cycloalkanes are also formed. In the case of larger transformation degree, arenes are formed [1, 9]. Some authors [12–14] attract the theory of cavitation phenomena in liquid phases and dispersions to explain the mechanisms of oil product transformation during MT.

EXPERIMENTAL

The subject of investigation was bitumen-saturated sandstone of the Olenek bitumen deposit situated at the North-East of the Siberian Platform.

In order to extract the maximal amount of bitumoids, sandstone was subjected to MT in AGO-2 set-up. The frequency of reactor rotation in translational motion was 1820 min^{-1}, treatment duration was 10 min. Milling tools were 60 steel balls 8 mm in diameter. Milling bodies and 30 g of the sample were charged into the mechanochemical reactor. The reactor was washed with argon many times to remove air. Experiments on MT of sandstone were carried out in hydrogen and argon environments. The reactors were filled with argon or hydrogen to the residual pressure equal to 1–1.5 atm.

To evaluate the effect of MT process on changes in the material and hydrocarbon composition of the organic part of sandstone, we carried out extraction of chloroform bitumoids (CB) from the initial sandstone and samples subjected to MT in argon and in hydrogen environment. Isolation of CB was carried out by means of hot extraction with chloroform in Soxhlet's apparatus.

To determine the material composition of CB, deasphalting with a 40-fold excess of *n*-hexane was carried out. Petrolenes were adsorbed on activated silica gel ASK, placed into the holder; oil species (concentrate of hydrocarbons) were sequentially extracted with *n*-heptane, gum species – with a mixture of ethanol with benzene (1 : 1) in Soxhlet's apparatus.

The procedure for the determination of group hydrocarbon composition was described in [15]. The HC concentrate was separated into fractions of saturated HC, mono-, di-, tri- and polyarenes. Monoaromatic cyclic HC are represented by the compounds of benzene series, diaromatic ones by the compounds of naphthalene series, triarene fractions are represented by the compounds of phenanthrene and anthracene series.

The individual composition of HC was determined with a Shimadzu GCMS-QP5050 gas chromatograph coupled to a quadrupole mass spectrometer by means of multiple ion monitoring (MIM) scanning mass chromatograms over characteristic ions in the mode of temperature programming on a capillary quartz column DB5-MS with the size 30 m × 0.32 mm. The fractions of saturated HC were analyzed in the mode of temperature programming from 50 to 290 °C at a rate of 4 °C/min, the final temperature was maintained at the constant level for 25 min. Carrier gas was helium. In the analysis of the fractions of aromatic HC, the mode of linear temperature programming from 80 to 290 °C at a rate of 2 °C/min was applied; the final temperature was maintained constant for 25 min. The composition of *n*-alkanes and isoprenoid HC was determined on the basis of the characteristic ion m/z 57, alkyl benzenes – with ions m/z 91, 105, 119, alkyl naphthalenes – with ions m/z 178, 192, 206. Identification of the peaks in chromatograms was carried out by comparing retention times of individual compounds and the components under analysis, and also with the help of the data of the mass spectra library.

Analysis of the gas mixture was carried out with Chromatron GHCF 18.3 gas chromatograph.

The detrital part of sandstone of the Perm deposit from Olenek deposit has the following composition: quartz 30–54 %, feldspar (potassium, acidic and neutral plagioclases) 15–25 %, rock debris (mainly quartz greywackes) 28–42 %. The average chemical composition of the trials (averaged over sampling 10 trials), %: SiO_2 82.06, TiO_2 0.36, Al_2O_3 8.39, Fe_2O_3 1.21, MnO 0.03, MgO 0.36, CaO 0.45, Na_2O 1.27, K_2O 2.81, P_2O_5 0.04. In our experiments, MT of oil-like substances was carried out in the presence of the mineral part, the major components of which are represented by silicon, iron, and calcium.

RESULTS AND DISCUSSION

The data on the composition of gaseous products formed during MT of sandstone are shown in Table 1. One can see that they con-

TABLE 1

Composition of gaseous products of the mechanical treatment of the samples of bitumen-saturated sandstone

Treatment environment	Concentration, vol. %					
	H_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	CO_2
Argon	80.70	17.65	1.43	0.17	0.05	–
Hydrogen	87.08	12.27	0.51	0.09	0.05	–

tain hydrogen and hydrocarbon-containing gases C_1–C_4.

The concentration of CB in the initial sandstone is 5.6 mass % (Table 2). The data of elemental analysis of the initial sample provide evidence that it contains carbon 75.3 %, hydrogen 9.3 %, nitrogen 0.8 %, and sulphur 3.6 %. As a result of MT of sandstone in the atmosphere of hydrogen, the yield of bitumoid decreased to 4.8 %, while it argon it decreased to 2.8 %. A decrease in the yield of butumoid is likely to be due to the formation of gaseous products. Unfortunately, within the existing apparatus arrangement of the process, it turned out to be impossible to estimate the amount of the formed gas.

The analysis of the material composition of bitumoids provides evidence that the concentration of pyrobitumen and oil decreased in the bitumoid obtained after MT of sandstone, while the gum content increased substantially in comparison with the concentrations of these components in the bitumoid of initial sandstone (see Table 2). It is necessary to stress that the total content of gum-pyrobitumen components in the bitumoid of the initial sample and the sample after MT in the atmosphere of argon is the same. An increase in the gum content in the bitumoid of the treated sample is likely to be due to destruction of pyrobitumen components. As a result of this destruction, the formation of gum species occurs; these gum species are oil components with smaller molecular mass. The material composition of the bitumoid of sandstone after MT in the atmosphere of hydrogen changed, too, though the change was not so substantial as that for the sample treated in the atmosphere of argon (see Table 2).

Mechanical treatment also causes changes of the group hydrocarbon composition of bitumoids (see Table 2). For instance, the concentrations of saturated HC, tri- and polyarenes decreases in the samples after MT both in the atmosphere of argon and in hydrogen. As a result of MT of the sample in the atmosphere of argon, the concentration of mono- and diarenes increase, which may be due to dehydrogenation of naphthene HC or destruction of high-molecular gum-pyrobitumen compounds. This is indicated by the fact that hydrogen com-

TABLE 2

Composition of bitumoids of the initial and mechanically treated sandstone samples

Fractions	Sample		
	Initial	After treatment in the atmosphere of:	
		argon	hydrogen
Material composition of bitumoids, mass %			
Oil	39.2	38.3	32.9
Gum species	28.2	40.2	32.3
Pyrobitumen	32.5	20.7	33.4
Group hydrocarbon composition, mass % (per bitumoid)			
Saturated HC	22.4	21.7	18.7
Monoaromatic HC	3.4	4.9	4.2
Diaromatic HC	3.7	4.0	2.7
Tri- and polyaromatic HC	9.7	7.8	7.4
Yield of bitumoid, mass %	5.6	2.8	4.8

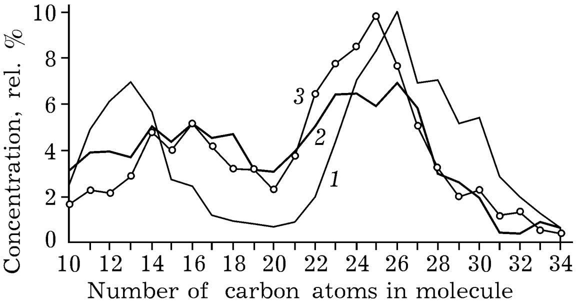

Fig. 1. Molecular mass distribution of n-alkanes of bitumoids of the initial (*1*) and mechanically treated samples in the atmosphere of argon (*2*) and hydrogen (*3*).

prises a substantial fraction of gaseous products of reaction during MT in the atmosphere of argon. During MT in the atmosphere of hydrogen, the fraction of diarenes decreases in comparison with their content in the bitumoid of the initial sandstone.

Analysis of the mass fragmentograms over the characteristic ion m/z 67 of the fractions of saturated HC of bitumoids of the initial sample and mechanically treated one provides evidence that they include n-alkanes with the number of carbon atoms 10 to 34 per molecule (Fig. 1). For the bitumoid of the initial sample, the molecular mass distribution (MMD) of n-alkanes has the bimodal character with the maxima corresponding to C_1 and C_{26} n-alkanes. After MT of sandstone, both in the atmosphere of argon and in hydrogen, we observe some changes in the character of MMD of n-alkanes. As a result of MT, the content of low-molecular (LM) n-alkanes increased in comparison with the content of high-molecular (HM) n-alkanes. This is evidenced by the values of LM/HM and n-C_{27}/n-C_{17} ratios (Table 3). The most substantial changes are observed for the composition of saturated HC of bitumoids after MT of sandstone in the atmosphere of argon.

In addition, MT leads to a decrease of Pr/Ph and Pr/n-C_{17} ratios in comparison with those for the initial sandstone (Table 3), which may be the evidence of destruction of pristine under the experimental conditions. In the initial bitumoid, the concentration of even n-alkanes exceeds the concentration of odd ones (the index CPI-1 = 0.88), while for bitumoids of the sample after MT CPI-1 = 1.0.

TABLE 3

Characteristics of the composition of saturated hydrocarbons of bitumoids of the initial and mechanically treated samples

Parameters	Samples		
	Initial	After treatment in the atmosphere of:	
		argon	hydrogen
Pr/Ph	1.6	1.0	0.6
Pr/C_{17}	0.6	0.6	0.4
Ph/C_{18}	0.5	0.5	0.8
CPI-1*	0.88	1.02	1.02
HM/BM**	0.5	0.8	0.5
n-C_{27}/n-C_{17}	7.3	1.3	2.4

*CPI-1 = S[(C_{25} + C_{27} + C_{29} + C_{31})/(C_{24} + C_{26} + C_{28} + C_{30}) + (C_{25} + C_{27} + C_{29} + C_{31})/(C_{26} + C_{28} + C_{30} + C_{32})].

**LM/HM = (n-C_{10} + ... + n-C_{20})/(n-C_{21} + ... + n-C_{36}).

In the fractions of cyclic monoaromatic HC of bitumoids of the initial sample and the sample after MT, naphthene-substituted compounds of benzene series prevail. This is confirmed by the mass fragmentograms of monoarene fractions with characteristic ions m/z 91, 105, 119, which look like broad unresolved “naphthene humps” without any indices of the presence of the peaks of alkyl-substituted benzenes (Fig. 2).

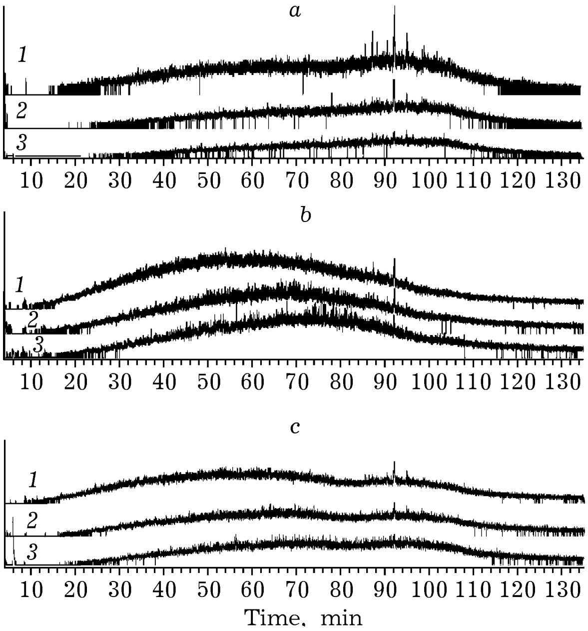

Fig. 2. Mass fragmentograms of the fractions of monoarenes of bitumoids of the initial (*a*) and mechanically treated samples in the atmosphere of argon (*b*) and hydrogen (*c*), m/z: 91 (*1*), 105 (*2*), 119 (*3*).

In the fractions of di- and triaromatic HC of bitumoid of the initial sandstone, we identified naphthalene (*m/z* 128), 2- and 1-methylnaphthalene (*m/z* 156), phenanthrene (*m/z* 178) (Fig. 3, *a*). The concentration of trimethylnaphthalenes is so low that we failed to identify them. We also did not detect methyl- (*m/z* 192) and dimethylphenanthrenes (*m/z* 206) in the bitumoid of the initial sandstone.

The ratio of naphthalene (N) to methyl- (MN) and dimethyl- (DMN), trimethyl- (TMN) substituted naphthalenes, phenanthrene (P) and methylphenanthrene (MP) was chosen as the criterion of changes in the composition of di- and triarenes of bitumoids of the initial sandstone and mechanically treated one (Table 4, Fig. 4). In the bitumoid of initial sandstone, MN content (N/MN = 0.63) and P content are higher in comparison with N content (N/P = 0.8), while N content is much higher than DMN content (N/DMN = 1.1).

In addition to N, MN, DMN and P, in the fraction of di-and triarenes of bitumoid of the sample after MT we identified TMN and MP that were absent from the bitumoid of the initial sandstone (see Fig. 3, *b*). It is necessary to stress that N content decreased sharply, which is confirmed by the ratio N/P = 0.07 (see Fig. 4). The ratios of N content to other components of this fraction are also characterized by low values.

The distribution of alkyl-substituted N and P in bitumoid of the sample after MT in the

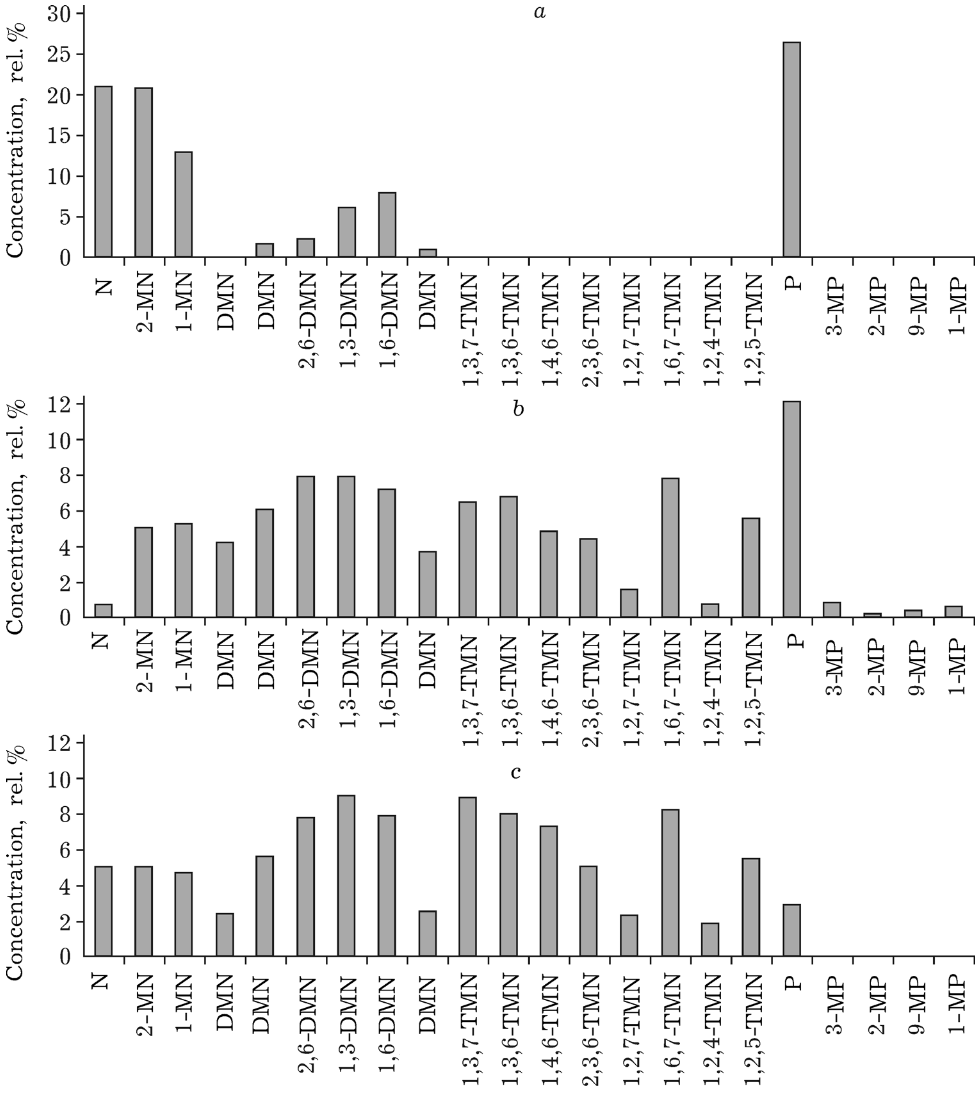

Fig. 3. Distribution of alkylnaphthalenes and alkylphenanthrenes in bitumoids of the initial (*a*) and mechanically treated sandstone samples in the atmosphere of argon (*b*) and hydrogen (*c*).

TABLE 4

Group composition of alkylnaphthalenes and alkylphenanthrenes of bitumoids in the initial and mechanically activated samples, rel. %

Compounds	Samples		
	Initial	After treatment in the atmosphere of:	
		argon	hydrogen
Naphthalene	21.1	0.7	5.1
Methylnaphthalene	33.6	10.3	9.7
Dimethylnaphthalene	19.2	36.9	35.1
pTrimethylnaphthalene	–	37.9	47.0
Phenanthrene	26.3	12.1	2.9
Methylphenanthrene	–	2.0	–
Dimethylphenanthrene	–	–	–

atmosphere of hydrogen differs from their distribution in bitumoids of the initial sample and the sample treated mechanically in the atmosphere of argon (see Fig. 3, *c*). The ratio N/P = 1.8 is maximal for the studied samples, which is the evidence of the predominance of N content over P. The ratio N/MN = 0.53 is close to that for the initial bitumoid.

CONCLUSION

Thus, it was established that profound transformations of bitumoid, the organic component of bitumen-saturated sandstone, occur during its MT.

A decrease in the concentration of bitumoids after MT is likely to be connected with the formation of gaseous products that are a mixture of hydrocarbon-containing gases C_1–C_4 and hydrogen. During MT of sandstone in the atmosphere of argon, substantial amount of hydrogen is formed. Changes in the material composition are due to the destruction of gum-pyrobitumen components and condensation of the intermediate products of decomposition.

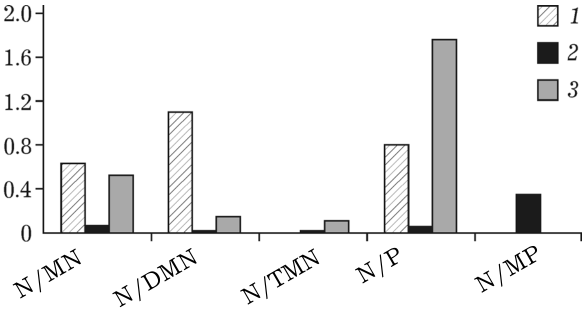

Fig. 4. Changes of some parameters of the composition of alkylnaphthalenes and alkylphenanthrenes in bitumoids of the initial (*1*) and mechanically treated samples in the atmosphere of argon (*2*) and hydrogen (*3*).

Changes in the individual and group composition of saturated and aromatic hydrocarbons are likely to be connected with the decomposition, cyclization and alkylation reactions. The direction of these reactions depends on the gas medium in which MT is carried out. Undoubtedly, the effect of the mineral component of sandstone on the changes of the composition of MT products is substantial.

Acknowledgement

Authors thank N. V. Popov from the Institute of Petroleum Chemsitry, SB RAS, for carrying out analysis of the gaseous products.

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