

EDN: OQMKGY

УДК 544.54:665.6–405

Electron Beam Impact on Petroleum Asphaltenes

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Received 12.06.2022, received in revised form 16.12.2022, accepted 24.01.2023

Abstract. The paper presents the results of the impact of an electron beam on the asphaltenes of oil from the Nurlatskoye field in an atmosphere of air, argon, hydrogen, and propane-butane mixture. The most noticeably changes in macrostructural parameters of asphaltenes are observed after beam treatment in a propane-butane mixture. The average number of stacking sheets and the size of the aromatic cores increases and the interlayer distance between saturated fragments changes. An increase in the number of aromatic rings in the sheet and a decrease in the share of saturated fragments may suggest the processes of destruction and aromatization of saturated structures, which is confirmed by an increase in the aromaticity factor. Analysis of the group composition of this sample showed the presence of paraffin-naphthenic and aromatic hydrocarbons, and resins. According to the data of thermogravimetric analysis, asphaltenes lose mass more intensively after treatment with an electron beam in a propane-butane atmosphere, which is most visible in the range from ~ 250 to 510 °C.

Keywords: electron beam, resins, asphaltenes, air, argon, hydrogen, propane-butane mixture.

Acknowledgments. This work was supported by the Ministry of Science and Higher Education of the Russian Federation (Registration Number 121031500046–7).

Citation: Neyfel'd, A.L., Savinykh, Y.V., Kopytov, M.A., Orlovsky, V.M. Electron beam impact on petroleum asphaltenes. J. Sib. Fed. Univ. Chem., 2023, 16(1), 59–65. EDN: OQMKGY



Воздействие электронного пучка на асфальтены нефти

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Аннотация. В работе представлены результаты воздействия электронного пучка на асфальтены нефти Нурлатского месторождения в атмосфере воздуха, аргона, водорода и пропан-бутановой смеси. Наиболее заметно параметры макроструктуры асфальтенов меняются после обработки пучком в среде пропан-бутановой смеси. Увеличивается среднее число слоёв в пачке, размер ароматического ядра, меняется межслоевое расстояние между насыщенными фрагментами. Увеличение количества ароматических колец в слое и снижение доли насыщенных фрагментов могут указывать на процессы деструкции и ароматизации насыщенных структур, что подтверждается увеличением фактора ароматичности. Анализ группового состава этого образца показал наличие парафино-нафтеновых, ароматических углеводородов и смол. По данным термогравиметрического анализа, асфальтены после обработки пучком электронов в атмосфере пропан-бутан более интенсивно теряют массу, что наиболее заметно в области от ~ 250 до 510 °С.

Ключевые слова: пучок электронов, смолы, асфальтены, воздух, аргон, водород, пропан-бутановая смесь.

Благодарности. Эта работа была поддержана Министерством науки и высшего образования Российской Федерации (регистрационный номер 121031500046–7).

Цитирование: Нейфельд, А.Л., Савиных, Ю.В., Копытов, М.А., Орловский, В.М. Воздействие электронного пучка на асфальтены нефти. Журн. Сиб. федер. ун-та. Химия, 2023, 16(1). С. 59–65. EDN: OQMKGY

Introduction

Electron irradiation as a method of delivering energy to a target molecule ensures that most of the energy is absorbed by the electronic structure of the molecule. This leads to the efficient formation of reactive particles capable of initiating chemical reactions [1]. Numerous works dealing with the exposure of oil hydrocarbons (HC) to electron beams show that the products formed during radiolysis of HC can be divided into three main groups: products of destruction or degradation with a molecular weight less than that of the initial HC, isomerization products, and compounds with higher molecular weight. Thus, the viscosity of oil with a high content of aromatic hydrocarbons increases due to the recombination of macroradicals of aromatic rings and the formation of polyphenylenes. In the case of a high content of paraffin hydrocarbons in oil, its exposure to the electron beam leads to a decrease in oil

viscosity because of alkyl chain destruction [2]. Comparison of the results of radiation-thermal cracking of bitumen samples [3] with methods such as thermal, thermal-catalytic, and ozone-thermal cracking showed that radiation provides a higher yield of oil fractions. Electron beam irradiation was considered as a way to partially improve the quality of high-viscosity oils [4, 5]. The authors of these works carried out a Monte Carlo simulation of the process of electron beam treatment of multiphase and single-phase oil hydrocarbons at different temperatures. It was shown that the destruction of hydrocarbons exposed to an electron beam is non-linear according to temperature. It was shown that electron-induced thermal cracking of high-asphalt oils leads to samples with a lower viscosity than in cases of thermal cracking [6]. To select the optimal conditions, the effect of temperature on the productivity of radiation-thermal cracking was investigated [7]. It is shown that the effective impact of the electron beam on heavy deasphalted oils begins at temperatures above 120 °C.

The study of the electron beam impact was conducted mainly in oils and oil products. There is a lack of data on the effect of exposure of individual oil components to electron beam. The effect of an electron beam on high-molecular compounds of oil (resins and asphaltenes) is scarcely studied.

The purpose of this work is to determine the effects of exposure of asphaltenes to the electron beam under atmosphere of various gases.

Methods and materials

Asphaltene samples were isolated from the oil sampled in the Nurlatskoye field as a result of precipitation with 40-fold hexane volume according to the standard ASTM D 4055.

An ‘Astra’ pulsed high-current electron accelerator was used as a source of an electron beam for processing hydrocarbons [8]. Accelerator parameters are as follows: electron kinetic energy is 90 keV, beam current density 65 A/cm², beam energy 0.2 J per pulse, full width at half maximum of the output current pulse duration is 2 ns, pulse repetition rate is 5 pulses/sec. The test samples were irradiated in a stainless steel cuvette with an inner diameter of 40 mm and a depth of 15 mm at 150 °C for 15 minutes at a standard dose of 7.56 kGy in an atmosphere of air, argon, hydrogen, and propane-butane (55:45). Asphaltenes are located at the bottom of the cuvette in an even layer, the amount of the substance is 50*10⁻³ kg.

The analysis of the groups composition (SARA) of samples were carried out by the method of gradient displacement liquid adsorption chromatography on silica gel. The samples were analyzed for the content of paraffin-naphthenic hydrocarbons (PNH), aromatic hydrocarbons (ArH), resin (Rn) and asphaltenes (As). The samples were separated using a “Gradient” instrument manufactured by Bash NINP [9].

X-ray phase analysis (XRD) of asphaltene powder samples was performed using a D 8 Discover X-ray diffractometer (Bruker, Germany) with monochrome CuK α radiation ($\lambda = 1.54184 \text{ \AA}$). Scanning was carried out in the range of 2θ angles from 0° to 90° at 20 °C. The diffraction patterns were processed using Origin Pro 8 and DIFFRAC EVA v1.3 (Bruker-AXS) software. The parameters were calculated according to the formulas given in [10–13].

The IR spectra were recorded in a KBr pellet in the range 400–4000 cm⁻¹ using a Thermo Scientific ‘Nikolet 5700’ FTIR Spectrometer equipped with a Raman module (Thermo Electron Corporation, USA).

Thermogravimetric analysis (TGA) of the samples was performed using a Q-1000 derivatograph. A sample weighed 100 mg was tested in an inert atmosphere (argon, flow rate 50 ml/min) with a furnace heating rate of 10 °C/min from room temperature to 850 °C.

Results and discussion

The exposure of the initial asphaltene sample to electron beam had minor effect on its degradation in air (Table 1). The amount of resins formed in an atmosphere of argon and hydrogen was small (4 %). Their formation is possible upon the elimination of peripheral fragments of asphaltenes.

In propane-butane atmosphere, in addition to resins, paraffin-naphthenic and aromatic hydrocarbons were detected. Resins and aromatic compounds could be formed as a result of the destruction of asphaltenes or be synthesized from propane and butane, while hydrocarbons could be resulted only from radical chain reactions [15].

The changes in the IR spectra were observed only for the sample treated with an electron beam in air. As a result of the oxidation of hydrocarbon chains, absorption bands appeared at 1703 cm^{-1} (carbonyl group) and 3147 cm^{-1} (hydroxyl group) [14].

Fig. 1 shows the diffraction patterns of the initial asphaltenes and those after treatment with an electron beam in a propane-butane medium. A pronounced γ -band in the region $2\Theta = 19^\circ$ suggests the presence of saturated structures in the initial asphaltenes. The reduction in the content of saturated structures in the macromolecule of these asphaltenes is indicated by a decrease in the intensity of the γ -band relative to the 002 band in the region $2\Theta = 26^\circ$, which is characteristic of condensed aromatic layers. Such a decrease in the intensity was observed only for the sample processed in the propane-butane mixture.

The parameters of the macrostructure of asphaltenes and coke, calculated from the data of X-ray phase analysis, are shown in Table 2. The macrostructural parameters of asphaltenes change most noticeably after beam treatment in a propane-butane mixture. The average number of layers in a stack (M) increases from 4.5 to 5.1, while the size of the aromatic core increases from ~ 24.7 of aromatic rings per layer to ~ 32.3 . The noticeable changes in interlayer distance (dm) and the distance between the saturated fragments (dr) are observed. These changes (an increase in the number of aromatic rings in the layer and, possibly, a decrease in the proportion of saturated fragments) may suggest the processes of destruction and aromatization of saturated structures, which is confirmed by an increase in the aromaticity factor f_a^{XRD} .

TGA data show that the asphaltene sample loses mass more intensively after treatment with an electron beam in a propane-butane mixture. This is most visible in the region from ~ 250 to $510\text{ }^\circ\text{C}$ (Fig. 2). The maximum rate of thermal degradation in the initial sample reaches its maximum at a temperature of $430.2\text{ }^\circ\text{C}$, while in a propane-butane atmosphere – at $433.2\text{ }^\circ\text{C}$. The most pronounced

Table 1. Group composition of samples after exposure of asphaltenes from Nurlatskaya oil to electron beam

sample in the atmosphere:	Content, wt%			
	PNH	ArH	Rn	As
Original	0	0	0	100
Air	0	0	0	100
Argon	0	0	4	96
Hydrogen	0	0	4	96
Propane-butane	8	6	9	77

PNH — saturated (paraffin-naphthenic) hydrocarbons; ArH — aromatic hydrocarbons; Rn — resins; As — asphaltenes

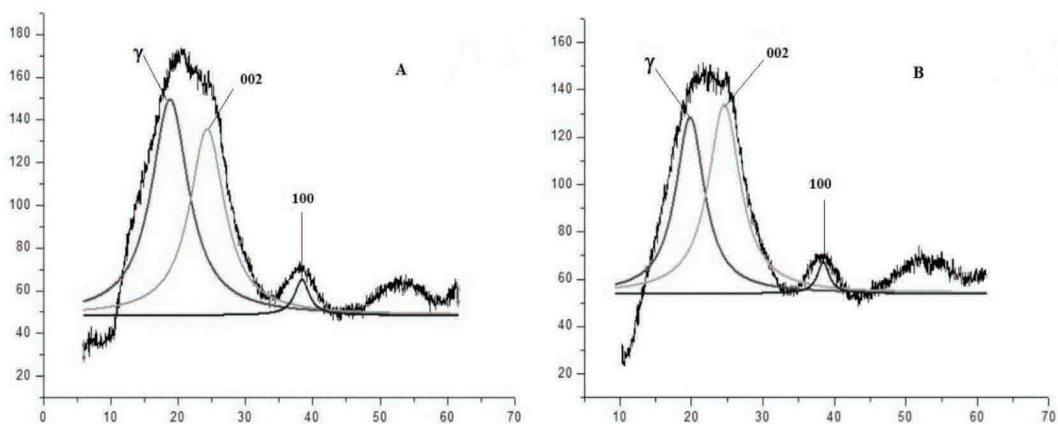


Fig. 1. X-ray diffraction patterns of the initial sample (A) and sample under propane-butane atmosphere (B)

Table 2. Macrostructural parameters of asphaltenes

Sample in atmosphere	Parameters							
	dm, Å	dr, Å	Lc, Å	M	La, Å	Na	f_a^{XRD}	ϕ_a
Original	3,66	5,90	12,90	4,53	65,90	24,71	0,45	0,29
Air	3,69	5,92	12,48	4,38	57,70	22,01	0,43	0,26
Argon	3,67	5,86	13,27	4,61	61,97	23,24	0,48	0,32
Hydrogen	3,67	5,82	13,64	4,72	66,48	24,93	0,44	0,28
Propane- butane	3,62	5,60	14,96	5,13	86,04	32,26	0,55	0,41

Where: dm — interlayer distances in packs, dr — distance between saturated fragments of molecules, Lc — average thickness of packs, M — average number of layers in a pack, La — average diameter of flat aromatic fragments of molecules stacked in packs, Na — number of aromatic rings in a layer, f_a^{XRD} — aromaticity factor, ϕ_a — level of clustered organization of carbon atoms

endothermic effects for the initial sample may be observed at a temperature of 418.9 °C to 509.7 °C and within a temperature range from 411.4 to 505.3 °C for a sample in a propane-butane atmosphere. As a rule, at temperatures of 410–420 °C, thermal degradation processes begin to occur, while at temperatures above 500 °C coking processes can occur with a slow weight loss. The increase in the rate of weight loss during thermal analysis of asphaltene samples obtained after exposure to an electron beam in a propane-butane mixture, in comparison with other samples, can be explained by the loss of hydrocarbon components adsorbed on it.

The results obtained show the resistance of asphaltenes to the electron beam impact. This may be due to the fact that asphaltenes contain derivatives of polycondensed aromatic compounds, which, having a high electron affinity and capturing slow electrons, lead to the damping of radical and radical ion reactions in the organic mass.

Conclusions

The results of the study showed that an exposure to low intensity electron beam (90 keV) does not lead to the destruction of chemical bonds in petroleum asphaltenes. When exposed to an electron beam,

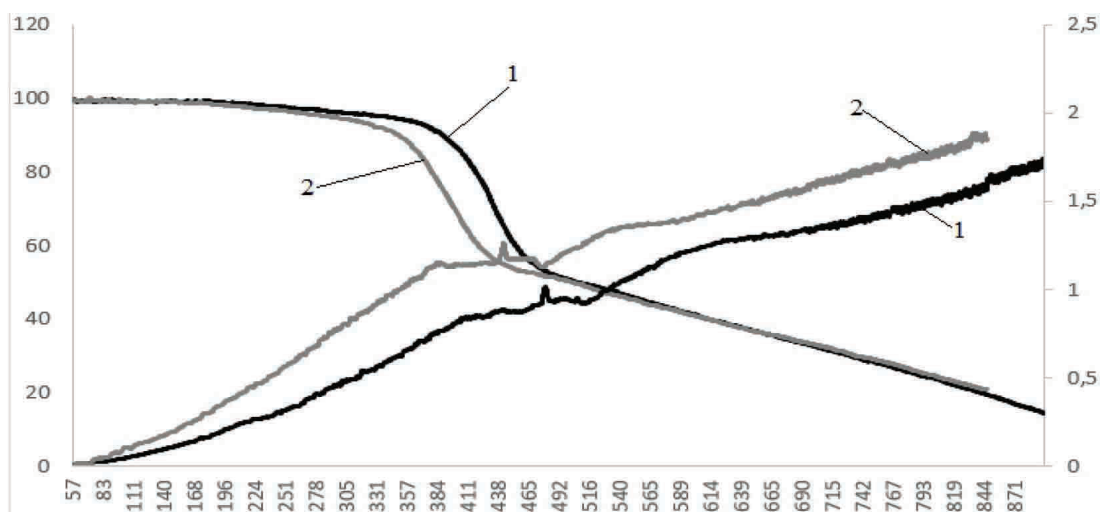


Fig. 2. TGA curves of initial asphaltenes (1) and asphaltenes treated with an electron beam in a propane-butane atmosphere (2)

a slight oxidation of asphaltenes in the air atmosphere is observed. In a neutral and reducing atmosphere the formation of a small amount of resins is observed. The macrostructural parameters of asphaltenes change most noticeably after beam treatment in a propane-butane mixture. According to TGA data, after treatment with an electron beam in a propane-butane atmosphere, asphaltenes lose mass more intensively in the region from ~ 250 to 510 °C. According to XRD data, the average number of stacking sheets and the size of the aromatic cores increase in this sample and the interlayer distance between saturated fragments changes. An increase in the number of aromatic rings in the sheet and a decrease in the share of saturated fragments may suggest the processes of destruction and aromatization of saturated structures, which is confirmed by an increase in the aromaticity factor. The process of destruction of asphaltene after treatment with an electron beam in a propane-butane atmosphere is evidenced by the appearance of paraffin-naphthenic and aromatic hydrocarbons and resins in the sample.

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