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PLASMA-CHEMICAL DECOMPOSITION OF HYDROCARBONS ON THE BASIS OF THE MICRO-ARC DISCHARGE WITH DISC ELECTRODES ROTATING IN THE BULK OF RAW MATERIALS

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An innovative plasma-chemical hydrocarbon processing reactor has been developed. It is based on the interaction of nonequilibrium gas-discharge plasma with hydrocarbons in the bulk of a raw material. The results of experiments have shown that nonequilibrium gas-discharge plasma of micro-arc discharge, initiated in the bulk of hydrocarbon raw materials, is a unique tool for their processing. It is shown that this method allows not only decomposing hydrocarbons into light fractions, but also simultaneous obtaining fullerenes and nanotubes.

Keywords: plasma-chemical synthesis, discharge in a liquid, micro-arc discharge, hydrocarbons, nanostructures.

INTRODUCTION

Nowadays technologies of processing of high-viscosity heavy oils into a *synthetic* oil developed in the world are mainly based on a combination of classical methods of processing of oil residues, such as coking, cracking, hydrotreating, and sulfur removal. As a rule, typical schemes of processing of heavy hydrocarbon raw materials at the initial stage include the atmospheric and vacuum distillation unit after which the tar, depending on the technological purposes, is subjected to secondary processing, including deasphalting, coking, visbreaking, or their combination with subsequent hydrotreating of the obtained gasoil and gasification of vat residues. At the same time, many scientists agree that the specific properties and complex structure of raw heavy hydrocarbon materials make classical methods of their processing ineffective. Therefore, one of the promising methods of processing of raw hydrocarbon materials are plasma-chemical ones whose advantage is the possibility to influence on and to control over the chemical reactions [1].

It should be noted that over the last few years, the plasma-chemical methods of processing of raw hydrocarbon materials have been studied by many researchers. Here the scientific groups headed by Yu. A. Lebedev, B. Shokri, S. Nomura, B. A. Timerkaeva *et al*. [2–14] should be mentioned. In many works it was pointed out that in this case, the nonequilibrium gas-discharge plasma is more promising. In particular, the chemical processes proceeding in nonequilibrium plasma differ from those in equilibrium plasma and from thermal processes and processes in the presence of catalysts by a number of specific features that allow one to increase the efficiency of many chemical reactions. Controllability and selectivity of target products of plasma-chemical reactions are provided by regulation of the dwell time of raw materials in the reaction zone at the expense of regulation of the rate of inflow and volume of raw materials in the reaction chamber. Thanks to high concentrations of charged and excited particles and radicals, the chemical reactions proceed with extremely high rates.

In the last few years, the microwave discharges initiated in gas bubbles in liquid hydrocarbons: n-dodecane, benzene, cooking oil, lubricating oil, waste oil, siliceous oil, water comprising methylene blue, and n-heptane [6–14]

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attract special attention. Since the plasma is in the liquid, the efficiency of physical and chemical processes upon exposure to its active particles and radiation is high. For this reason, the rates of product formation are also high. However, the available data volume is insufficient for evaluation of prospects for application of such discharges. In all above-listed works, the microwave discharges were created by antennas of different types. The gas bubbles were formed either by liquid evaporation, gas (argon) sparging, or upon exposure to ultrasound. Here the difficulties connected directly with the microvale technology and initiation of micro-discharges in a liquid should be mentioned.

In connection with the foregoing, the presented work was aimed at initiation of a micro-arc discharge in the bulk of raw hydrocarbon materials for their processing.

DESCRIPTION OF THE EXPERIMENTAL SETUP AND RESULTS OBTAINED

The plasma-chemical setup (Fig. 1) comprises power supply source *4*, measuring devices *1* and *2*, two copper plate electrodes *8* and *13*, ballast resistance *3*, scraper *9* for cleaning of electrodes from solid deposits during experiments, cap *6*, and ceramic container *12* with raw hydrocarbon materials.

Electrodes *8* and *13* in the form of copper round discs 5 cm in diameter are located one above another at a distance such that steady-state micro-arc discharge burning is provided. Disc electrodes are fixed on a metal rod clamped to the cap with a plug. Electric motor *5* is located at the upper part of the cap and rotates the cap with electrodes using belt drive *10*. The metal scraper located inside the container beyond the zone of arc burning cuts off deposits from the electrodes which allows the setup to operate continuously for a long time.

On the cap surface there is microasperity *17* (the elevating mechanism for the lower electrode) providing contact of electrodes for arc ignition. The elevating mechanism is designed as follows: pin *18* rigidly clamped on a pulley which while rotating reaches the asperity on the cap and raises the shaft with cathode *13*. In order that scraper *9* that cleans the right electrode can also rise with the cathode, it is fixed on the shaft with bearing *16* above the pulley. An arc discharge is ignited when the electrodes are in contact; then the design falls down again. The proposed method prevents sticking of the electrodes and discharge attenuation. The rotating electrodes during arc burning are not heated because they are directly in raw materials; on the contrary, they are cooled.

A working liquid is poured into container *12* until plates (the cathode and the anode) are at a depth of several centimeters. The container is hermetically closed by the textolite cap. In the cap there is a hole to which gas outlet pipe *14* is connected. The volatile oil fractions through the pipe flow to gas collection tank *15*. In this case, black oil is used as a working liquid.

The electrodes rotated by the electric motor. The voltage is applied to the electrodes through special brush contacts. After establishment of the desired values of current and voltage, the setup continues to operate without human intervention. The advantage of the design is that it does not need cooling, because the electrodes have time to be cooled as a result of rotation in the bulk of black oil. In this case, the arc discharge constantly changes points of contact with electrodes.

Stable arc burning at a distance between the electrode of 0.5 mm was observed at currents of 0.1–1 A and voltages of 550–100 V. With these discharge parameters, hydrocarbons decomposed into easy fractions. During decomposition, the vapor-gas mixtures were continuously formed, and carbonaceous samples were formed in small amounts.

In the second series of experiments, the right electrode was fixed above the left electrode so that the distance between the discs was made equal to 1 mm. Stable burning of the micro-arc discharge at such interelectrode distance was observed at currents from 0.35 to 1.15 A and discharge voltages from 640 to 115 V. For these parameters, the gas-vapor mixture and carbonaceous formations were actively produced.

For an interelectrode distance equal of 1.5 mm, stable arc burning was reached only at currents exceeding 2 A. For a current of 2 A, the discharge voltage was equal to 840 V. These operating modes led to the formation on the electrodes of large amount of carbonaceous deposits. Thus, the process of deep decomposition of heavy hydrocarbon raw materials was accompanied by intense production of a gas and formation of soot on the electrodes. The amount of gas and soot depends on the applied voltage.

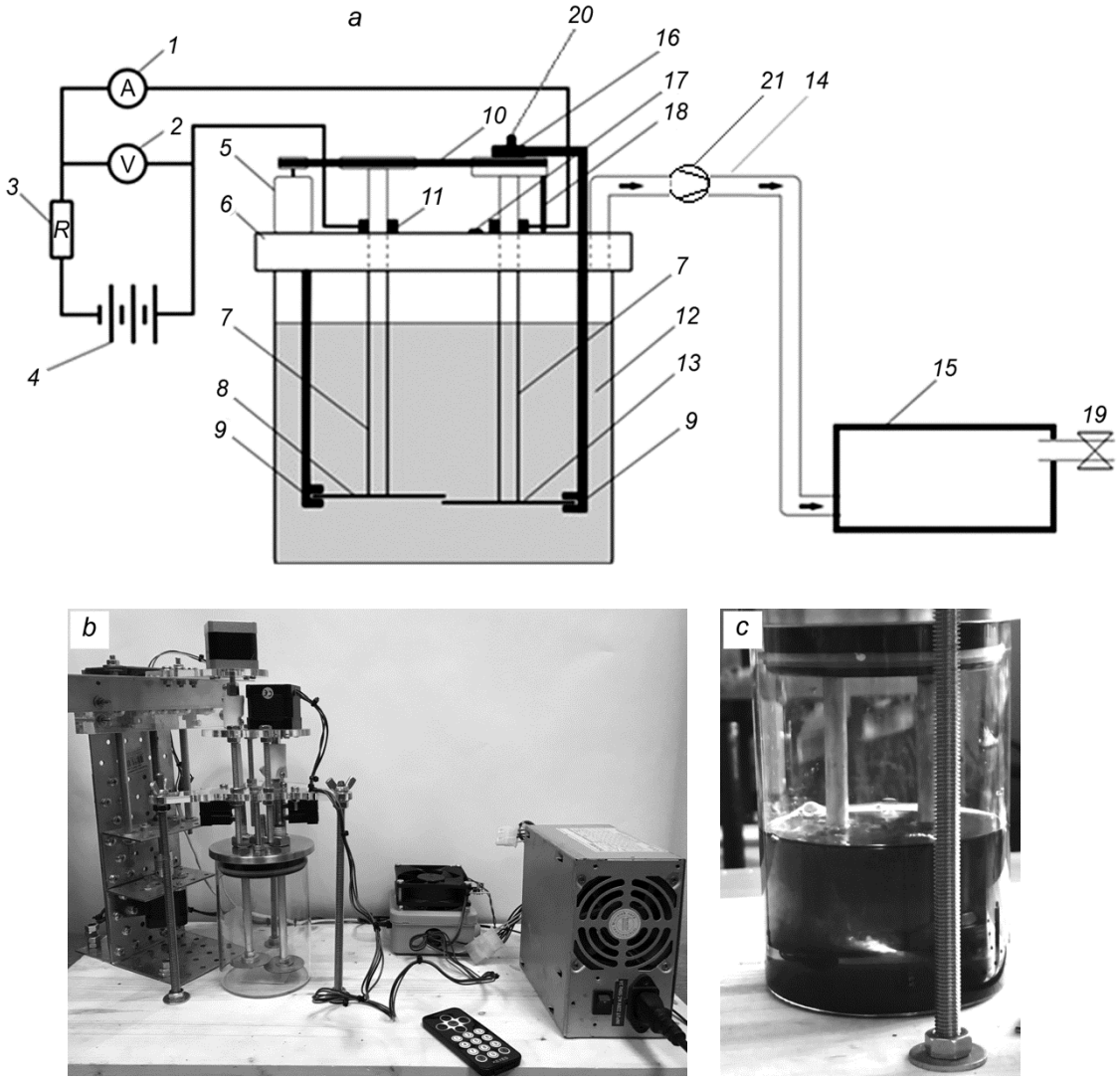

Fig. 1. Scheme of the setup with rotating electrodes for decomposition of raw hydrocarbon materials comprising ampermeter *1*, voltmeter *2*, ballast resistance *3*, power supply source *4*, electric motor *5*, cap *6*, axis *7*, anode *8*, scraper *9*, belt drive *10*, sliding contact *11*, container with raw materials *12*, cathode *13*, gas outlet pipe *14*, gas collection tank *15*, bearing *16*, microasperity *17*, rod *18*, gate *19*, reductor *20*, and compressor *21* (*a*). Photographs of the experimental setup (*b*) and the discharge in the bulk of a raw hydrocarbon material (*c*).

The products obtained during interaction of the gas-discharge plasma initiated in the bulk of hydrocarbon raw materials with this material were carefully analyzed. We here consider some results of this analysis. The light and volatile oil fractions formed in the process of plasma-chemical processing of black oil were analyzed on a Chromatec Crystal 5000.2 chromatograph. Results of this analysis are presented in Table 1.

The chromatographic analysis showed that the main products of decomposition of hydrocarbon raw materials were ethylene >40%, hydrogen 24%, and methane 7%. Carbonaceous deposits formed during experiment on the electrodes were analyzed using a scanning electron microscope; their images are shown in Fig. 2.

TABLE 1. Results of Chromatographic Analysis of Volatile Fractions

Group	Area	Height	Concentration	Detector
Ethylene	22908.011	4366.667	40.7763	TCD-2
Ethane	1757.163	304.803	0.5075	TCD-2
Helium	607.291	82.341	0.1377	TCD-3
Hydrogen	170170.29	11965.079	24.2153	TCD-3
Methane	11151.748	320.588	6.9832	TCD-3
C3	8224.724	905.049	1.904	TCD-2
C4	5300.193	207.962	1.0706	TCD-2
C5	1323.808	27.546	0.2137	TCD-2
C6	1086.32	13.701	0.1635	TCD-2

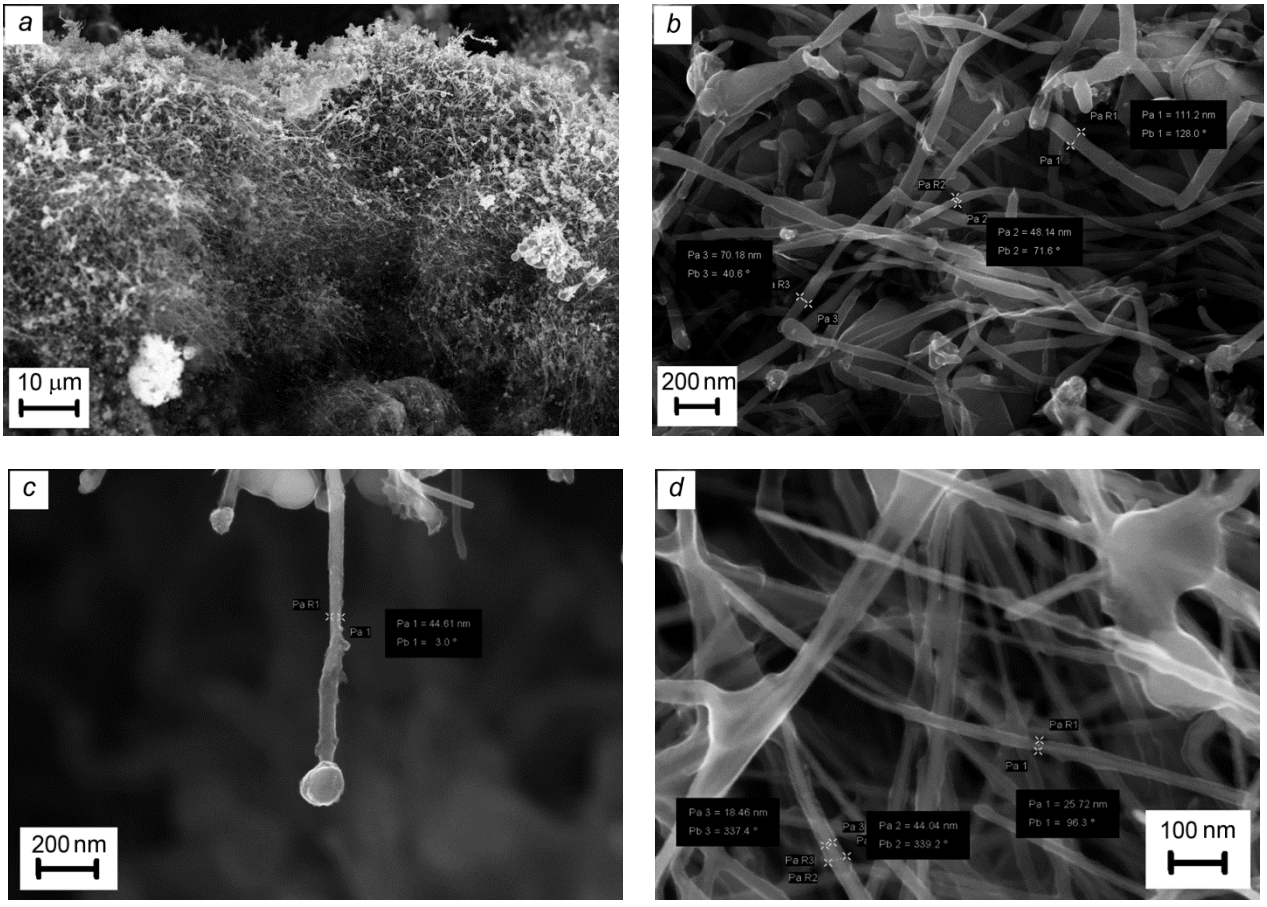

Fig. 2. SEM images of carbonaceous deposits with zoom ×3000 (*a*), ×77000 (*b*), ×125000 (*c*), and ×260000 (*d*).

As can be seen from the SEM images, a large number of carbon nanotubes (fibers) with different lengths and structures is contained in the deposit on the electrodes. The nanostructures were formed in chaotic order as threads closely weaved among themselves. The nanotube diameters fluctuated from 50 to 120 nm (Fig. 2*a*-*d*). The large nanotube diameter indicated their complicated structure. In some images, the nanotubes had multilayered structure. In Fig. 2*d*, multilayered nanotubes of "Russian nested doll" type can be seen. The nanotube has a diameter of 44.04 nm, and the nanotube inside it has a similar shape and a diameter of 18.46 nm.

Thus, carbon atoms are released upon bombardment by electrons, ions, and excited hydrocarbon particles. The formation of carbon atoms in plasma upon exposure to a strong electric field is a fundamentally new result; in this case, the process of obtaining fullerenes and nanotubes becomes controllable: Carbon atoms formed under such conditions possess electronegative properties, that is, they can join an electron and hence, can be controlled by the electric field. In the electric field, carbon ions move toward the anode and participate in the formation of carbon compounds. Depending on the initial nucleation centers on the anode or in the plasma volume, different nanostructures can be formed.

CONCLUSIONS

In this work, the possibility has been demonstrated of micro-arc discharge initiation in the bulk of liquid hydrocarbons for their processing. The performed series of experiments demonstrated that gas-vapor mixture and carbonaceous formations are intensly produced at interelectrode distance of 0.5 mm, currents of 0.1–1 A, and voltages of 550–100 V as well as at interelectrode distance of 1 mm, currents from 0.35 to 1.15 A, and voltages in the range from 640 to 115 V. The chromatographic analysis showed that the main products of decomposition of hydrocarbon raw materials were ethylene >40%, hydrogen 24%, and methane 7%. The electron microscope images showed that deposits on the electrodes contained a large number of carbon nanostructures. Thus, the results of our experiments have shown that the nonequilibrium gas-discharge plasma of micro-arc discharge initiated in the bulk of hydrocarbon raw materials is the unique tool for their processing: Heavy hydrocarbons decompose into easy fractions with simultaneous formation of carbonaceous nanostructures.

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