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APPLIED PHYSICS

Some Results from Studies of Microwave Discharges in Liquid Heavy Hydrocarbons

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Abstract—Some results from studies of microwave discharges in heavy hydrocarbons are presented. Microwave energy was introduced into liquid hydrocarbon via a coaxial line. The pressure above the liquid surface was equal to the atmospheric pressure. The discharge was ignited in a mixture of argon and hydrocarbon vapor. Argon was supplied through a channel in the central conductor of the coaxial line. The emission spectra of discharges in different liquid hydrocarbons were studied. It is shown that the emission spectra mainly consist of sequences of Swan bands, while radiation of other plasma components is on the noise level. Spectra of plasma emission are presented for discharges in liquid *n*-heptane, nefras, and C-9 oil used to produce chemical fibers. The rotational (gas) and vibrational temperatures are determined by processing the observed spectra.

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INTRODUCTION

In recent years, plasma in liquid has attracted considerable attention of researchers. This is explained by its possible promising applications in solving ecological problems and preparing various gas-phase and solid products [1–5]. Since plasma is produced in a gas bubble inside the liquid, the efficiency of physicochemical processes occurring under the action of active plasma particles and plasma radiation is fairly large. Accordingly, the formation rates of the resulting products are also large.

There is extensive literature on microwave discharges in different liquids: in water and water solutions [5–12]; in *n*-dodecane [13–16]; in benzene, commercial food butters, engine oil, and waste of food and engine oils [14]; in silicone oil [15]; in alcohol [17]; and in *n*-heptane [18, 19]. The combined effect of microwaves and ultrasonic waves was described in [13, 14].

Earlier, we carried out experiments with liquid alkanes C_nH_{2n+2} in a setup described in detail in [18, 19, 23]. It was a cubic metal chamber into which microwave energy was supplied from three magnetrons (2.45 GHz, 500 W) by means of rectangular waveguides. A vessel made of heat-resistant glass was placed in the chamber in which a quarter-wave resonant microwave antenna was installed (the antenna length was approximately 2 cm, which corresponds to a quarter wavelength in the hydrocarbon medium) on a metal base. The hydrocarbon (with a volume of ~50 mL) was poured in the vessel and completely covered the antenna. The space above the liquid surface was constantly washed by an argon flow. The discharge was initiated in the gas bubble at the end of the antenna. A gas bubble could be created artificially by feeding argon through a channel made in the antenna. In [19, 23], the emission spectra of alkanes in the apparatus described above were investigated. It is shown that plasma radiation contains only Swan emission bands $C_2(d^3\Pi_g - a^3\Pi_u)$. The processing of these bands shows that the gas temperature in the discharge is approximately 1700 K and the rotational temperature of C_2 molecules in the $d^3\Pi_g$ state is approximately 8000 K. After the addition of argon, the gas temperature decreases to 700 K, while the rotational temperature of C_2 molecules remains unchanged. Two-dimensional simulations of a discharge in liquid *n*-heptane [24, 25] in a coaxial system similar to that described below made it possible to estimate the electron density in the discharge, which was found to be on the order of 10^{14} cm^{-3}. The role of electron impacts in hydrocarbon decomposition can be important in the initial stage of the discharge. As the temperature of the gas rises, the role of thermal dissociation increases and it becomes the process that determines hydrocarbon decomposition.

In this work, the first results obtained using a setup with a coaxial input of microwave energy into liquid

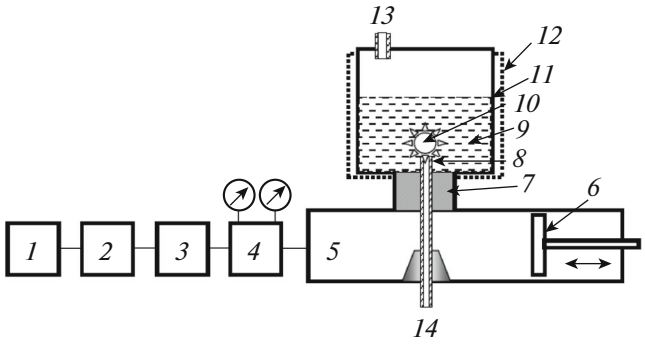

Fig. 1. Block diagram of the setup: (*1*) microwave generator, (*2*) circulator, (*3*) attenuator, (*4*) directional coupler, (*5*) coaxial-waveguide junction, (*6*) short-circuiting piston, (*7*) dielectric, (*8*) antenna, (*9*) liquid, (*10*) discharge region, (*11*) quartz reactor, (*12*) metal grid screen, (*13*) gas output, and (*14*) gas input.

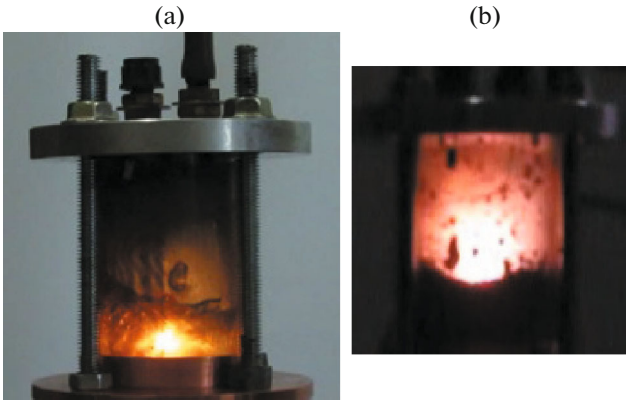

Fig. 2. (Color online) Photographs of microwave discharges in (a) liquid *n*-heptane and (b) hydroconversion product.

hydrocarbon are presented. Such devices are suitable for creating plasma in liquids [5]. In our experiments, we used hydrocarbons that differed significantly in their viscosities.

EXPERIMENTAL SETUP AND DIAGNOSTIC TECHNIQUES

Experiments were carried out using the setup whose block diagram is shown in Fig. 1. The microwave section consists of a microwave generator, circulator, water attenuator, directional coupler, spectrum analyzer, and an oscilloscope. The attenuator allows one to smoothly vary the input power in the range of up to 3 kW. The discharge section is a waveguide–coaxial junction, the central conductor of which serves as an antenna for supply of microwave energy into the discharge. A moveable short-circuiting piston was used for matching.

The discharge was ignited in a 55-mm-diameter quartz tube placed in a protective screen. The central electrode of the coaxial line is made of a copper tube with an outer diameter of 6 mm. Additional gases can be supplied through the channel in the electrode into the chamber. In this work, we used argon at a flow rate of 20 sccm. The experiments were carried out at a microwave power of up to 1 kW.

The discharge radiation was focused with the help of optics on the input aperture of the optical fiber directing radiation to the entrance slit of the AvaSpec 2048 spectrograph. The emission spectra in the wavelength range of 200–700 nm were recorded. The spectrum was relatively calibrated using an SI-8-200 tungsten lamp. The spectrum processing technique was described in detail in [23]. The discharge was visualized using a digital camera with a frame rate of up to 240 fps.

The discharge was ignited in various liquids: alkanes C_nH_{2n+2}, different technical oils (I-20, C-9, MC-20, I-50, M-9C, and VM-4 with a kinematic viscosity in the range of 6–11 mm^2/s), organic solvents (nefras C2 80/120), and an oil hydroconversion product with carbon and hydrogen contents on the order of 90 and 10%, respectively, at a low dilution with nefras. The volume of liquids was approximately 40 mL, which was sufficient for the end of the inner electrode of the coaxial line to be under the liquid surface. The pressure above the liquid surface was equal to the atmospheric pressure.

RESULTS AND DISCUSSION

Figure 2 shows photographs of a microwave discharge in liquid *n*-heptane and the hydroconversion product. It is seen from Fig. 2a that the discharge operates at the end of the inner coaxial conductor. The surface of the liquid is also seen.

The hydroconversion product (Fig. 2b) is opaque, and no plasma radiation is seen. Only the discharge glow above the liquid surface is visible. Dark spots in the photo are explained by the appearance of a solid black carbon-containing product on the surface of the quartz tube.

Figure 3 shows the three-dimensional carbon-containing structure formed at the end of the central conductor of the coaxial line in the experiment with the hydroconversion product. The black shining surface at the base of the coaxial is the remainder of the hydroconversion product after removal of its bulk from the discharge tube. It should be noted that such structures are also formed, although with a lower intensity, in discharges in oils.

The study of the emission spectra of a microwave discharge in different heavy liquid hydrocarbons under supply of argon through the central conductor of the coaxial line in the wavelength range 200–700 nm has shown that they have common features. As in the earlier experiments with other hydrocarbons

Fig. 3. Tree-like structure at the end of the electrode formed in a discharge in the hydroconversion product.

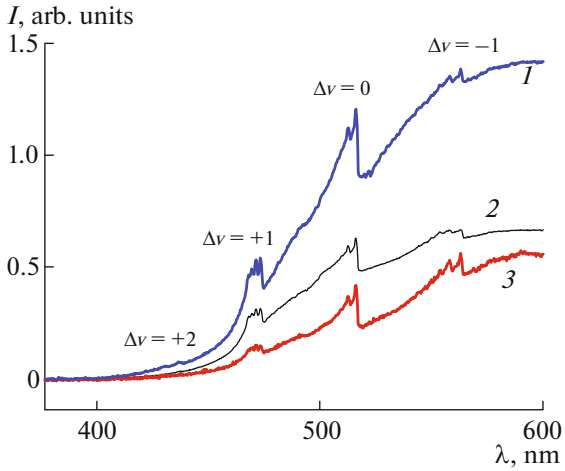

Fig. 4. (Color online) Examples of emission spectra of microwave discharges in liquid hydrocarbons: (*1*) C-9 oil, (*2*) *n*-heptane, and (*3*) nefras C2 80/120.

[23], the spectra mainly consist of different sequences of the Swan bands. Examples of spectra on an arbitrary scale are shown in Fig. 4 (the intensity scale is changed for illustrative purposes). The reason for the absence of lines of atomic hydrogen in the spectra can be the insignificant role of electron impact in the formation and excitation of radiative states [25]. We note that plasma is nonstationary and the formation of the solid phase and heating of the liquid take place in it. All this leads to the spatial inhomogeneity of the medium through which the radiation is recorded. In addition, the discharge itself is also nonstationary. The spectra shown in Fig. 4 are averaged over the observation time. Naturally, all this makes the spectra to be difficult to interpret.

The emission spectra allow one to estimate the gas and rotational temperatures in the discharge in heavy hydrocarbons according to the technique described in [23]. For all hydrocarbons, the gas temperature was in the range of 1000–1500 K, while the rotational temperature of C_2 molecules in the $d^3\Pi_g$ state was 6000–8500 K. These values agree with the data obtained for other hydrocarbons at the setup with a resonance antenna [23].

CONCLUSIONS

The first results from studies of microwave discharges in heavy hydrocarbons with different viscosities, including the hydroconversion product, are presented. Microwave energy was supplied into the liquid by means of a coaxial line. The pressure above the liquid surface was equal to the atmospheric pressure. Argon was supplied into the system through a channel in the central electrode. It is shown that, for viscous hydrocarbons, tree-type structures are formed on the central electrode of the coaxial line in the course of plasma processing. The plasma emission spectra are presented for plasma in liquid *n*-heptane, nefras C2 80/120, and C-9 oil used to produce chemical fibers. It is shown that the emission spectra coincide qualitatively and consist of sequences of the Swan bands. For all hydrocarbons, the gas temperature estimated from the Swan bands was in the range of 1000–1500 K, while and the rotational temperature of C_2 molecules in the $d^3\Pi_g$ state was 6000–8500 K.

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