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Microwave discharge in liquid hydrocarbons

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Discharges in liquids have attracted the attention of researchers and they are one of the priority areas in the study of the physics and application of low-temperature plasma [1, 2]. This is explained by both possible promising applications of such discharges in solving environmental problems, and using it to produce various gas-phase and solid products. All types of electrical gas discharges are used for these purposes, but the least explored are the microwave discharges. Current status of microwave discharges in dielectric liquids is given in [3]. This paper summarizes results of original studies of atmospheric-pressure microwave discharge in gas bubbles at the tip of the microwave antennas immersed in liquid alkanes (C_nH_{2n+2}, n = 7, 8, 10, 15, 16) differed in the boiling temperatures (from 98.42 ^oC to 286.79 ^oC). [4–10].

Experimental setup

Two experimental setups were used: the first one was based on the quarter wavelength antenna immersed in liquid hydrocarbon [4, 5, 10], and the second one was based on the coaxial line with the central conductor (antenna) immersed in liquid hydrocarbon for a particular length [6]. To obtain the maximum value of microwave field at the end of antennas it lengths were calculated from solution of Maxwell equations taking into account the geometry of discharge system and dielectric properties of hydrocarbons. This gives possibility to minimize the incident microwave power necessary to ignite and sustain the discharge. Microwave energy was delivered from a magnetron generator (frequency 2.45 GHz, microwave power below 1000 W). Discharge was non-stationary as the gas bubble, generated at the antenna end due to evaporation of liquid or by supplementary gas, is detached from the antenna end after plasma ignition and floated up. Plasma is disappeared as microwave field decreases with distance from antenna. The second reason of instability is saturation of liquid by carbonaceous solid products of plasma chemical reactions. These products effectively absorb microwaves and strongly decrease of microwave field in the antenna vicinity and thus decrease the probability of plasma ignition. This process leads to hydrocarbon heating and evaporation.

The system was oxygen free as argon gas was continuously blown through the space above the liquid surface. To simplify the discharge ignition additional argon could be introduced through the channel in antennas. The gas pressure above the liquid was close to atmospheric pressure. Microwave discharge was ignited in gas bubbles (hydrocarbons vapor or the mixture of these vapors with argon).

Plasma parameters (spectral composition, rotational and vibrational temperatures and temperature of solid products) were specified from plasma emission studied with spectrometer AvaSpec 2048 [5].

To characterize the solid phase we used a JEOL JSM-7500F high resolution field emission scanning electron microscope coupled with an INCA PentaFETx3 energy dispersive X-ray spectrometer (Oxford Instruments, UK). Raman spectra of the solid products were recorded with a RamanStation 400 (Perkin–Elmer, USA) Raman spectrometer furnished with a diode laser having λ_{ex} = 785 nm. FTIR-ATR spectra were acquired with a Tensor 27 (Bruker GmbH, Germany) FTIR spectrometer furnished with a Miracle (Pike Technologies Inc., USA) ATR attachment.

To obtain ^1H and ^{13}C NMR spectra of the solid phase, we used a Varian Unity Inova AS 500 spectrometer with probe A T3 HXY 3.2 mm was. A C/H atomic ratio in the solid phase was determined chromatographically after combustion of sample in the dynamic flash.

Sizes of residuals solid nanoparticles in a processed liquid hydrocarbons after centrifugation were studied with a Zetatrac laser analyzer (λ = 750 nm).

Processed liquid hydrocarbons were studied with GC/MS Thermo DSQ II device. The concentrated liquid sample (after evaporation) was studied with the same device and with IR-Fourier spectrometer Tensor II (Bruker GmbH, Germany).

Results and discussion

The only method for study of plasma properties in liquids is the emission spectroscopy. It was shown that emission spectra of plasma in all hydrocarbons contain only C_2 Swan bands ($d^3\Pi_g$–$a^3\Pi_u$) with rotational temperature 1000–1500 K and vibrational temperature of 7500 K. Addition of argon decreases the rotational temperature up to 600 K. Non of hydrogen atom or molecules emission was observed although hydrogen is the main gas phase product. Observed emission continuum can be attributed to the emission of solid particles produced in plasma and having the temperature of 4000 K [5].

The electron concentration in the discharge was estimated to be about 10^{14} cm^{-3} from 2D simulation of the MW discharge in liquid *n*-heptane [8, 9].

The solid carbon containing products, separated from processed liquid hydrocarbons by centrifugation (3000 rpm), are represented by particles having dimensions in the range of 100–200 nm. For all the products studied, Raman spectra have exhibited a set of necessary bands permitting to categorize these solids as a “damaged graphene”, and mainly not single-layered one [4, 10].

EDS analysis of the solid samples showed presence of carbon (80–90%), oxygen (2–15%) and copper (below 2%) atoms. Source of copper is the eroded copper antenna. The carbonaceous products were kept in air atmosphere before subjected to further analysis and absorbed oxygen is showed in analysis.

NMR spectra of solid products obtained from processed hydrocarbons reveal that generation of microwave plasma in liquid alkanes leads to strong aromatization and formation of various unsaturated molecular fragments in solid products.

Initially transparent colorless liquid hydrocarbons after processing and removal of solid particles become colored transparent yellow-brown. GC/MS analysis of hydrocarbon composition before and after treatment reveals no changes in the main composition of hydrocarbons. Only insignificant amounts (<1%) of polycyclic aromatic hydrocarbons are detected in absorption and luminescence spectra of liquid hydrocarbon after processing. The question is: where the solid particles are produced – in liquid hydrocarbon from the polyaromatic compounds or in the plasma region, how it was observed in numerous papers in gas phase plasma chemistry? Analysis of our experimental results leads to the conclusion that carbonaceous nanoparticles are produced in the region of gas bubble with microwave discharge near the tip of the antenna. Then the particles are transferred into the liquid. Convective flows emerging during heating the liquid hydrocarbon spread the solid particles over the entire volume of the liquid. After prolonged treatment of a hydrocarbon with the discharge, a tree-like structure can be formed on the antenna ending [6].

Liquid hydrocarbons after centrifugation contain solid nanoparticles with sizes ranged between 1 and 3 nm.

What is the role of electron impact in the processes in discharges in liquid hydrocarbons at atmospheric pressure? It is one of the key questions in plasma chemistry.

The role of the electron impact in the decomposition of n-heptane in microwave discharge in liquid n-heptane at atmospheric pressure has been investigated on the basis of two-dimensional self-consistent model for numerical modeling of the process of formation of gas bubbles during initiation of the microwave discharge [8, 9]. The developed model has an axial symmetry. The model is based on joint solution of the Maxwell equations, Navier-Stokes equation, heat equation, continuity equations for electrons (written in the ambipolar diffusion approximation) and the n-heptane concentration (including its thermal decomposition and dissociation by electron impact) and the Boltzmann equation for free electrons of the plasma. The calculations allowed describing the dynamics of the formation of gas bubbles in the liquid, to evaluate the role of electron impact in the decomposition of *n*-heptane, and to estimate the characteristic times of various processes in the system. The results of experiments are in agreement with the simulation results.

It was shown that the electron impact dissociation can take place only in the plasma bubble in vicinity of the antenna tip where microwave field strength has maximum value. The effect of electron impact is important in the *n*-heptane decomposition at times below 10^{-3} s and is negligible at time exceeds 10^{-3} s when the gas temperature exceeds 1000 K. For larger time the thermal decomposition of hydrocarbon prevails over others and the role of electron component is only in the gas heating.

This result gives possibility to explain why we did not see hydrogen in the emission spectra of discharge? It is known the emission of hydrogen lines and bands id provides by the electron impact whereas the emission of C_2-molecules is provided by the collisions of plasma heavy particles. Measurements of emission spectra were made with time delay against the switching of the discharge and thus the short period of prevalence of the electron impact was not seen.

Decrease of the pressure should lead to increase of the role of electron impact. This is why in known experiments with lower pressures the emission of hydrogen atoms was observed.

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