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ORIGINAL PAPER

Plasma reforming of liquid hydrocarbon in plasma-liquid systems

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Abstract. This paper presents the results of an experimental study of plasma-assisted reforming of ethanol into molecular hydrogen in a modified tornado type electrical discharge. Plasma acts as a catalyst and initiates fast chain reactions that do not progress under normal conditions. Passivation of the electrodes in the discharge chamber during the discharge operation prevents their erosion and increases the working time of the reactor.

Key words: plasma reforming • plasma chemical technologies • chemical conversion • plasma liquid systems

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Introduction

Recently, the development of new plasma chemical technologies often requires solutions not only for traditional tasks (high selectivity of transformation of substances, no pollution of the final product by plasma generator electrode material), but additional requirement – a high efficiency of plasma chemical conversion. The latter is connected with using the most expensive form of energy – electricity in plasma generation. It is well known that problem of the selectivity in plasma chemistry transformations is usually associated with the non-equilibrium plasma utilization [4]. However, the large number of different active species (electrons, ions, radicals, excited atoms and molecules, photons), even in a non-equilibrium plasma, yield the multichannel feature in chemical reactions. Therefore, some authors consider the solution of selectivity problem as a transition from traditional plasma systems with solid walls to the plasma-liquid systems (PLS). The latter has a direct contact between ionized gas and fluid [7].

PLS may solve the problem of electrode material removal. Special type of PLS has solid electrodes immersed in a liquid, so current through the liquid in such systems is connected with electrochemical processes near electrodes and at the liquid bulk. The choice of positive electrode with passivation effect on its surface leads to charges transport in electrochemical system by electrolyte ions only [1]. Any part of electrode material is not entering in an electrolyte. But similar processes in PLS are not investigated now.

A possible approach to significant improvement of energetic efficiency in plasma chemical reactions is the transition to plasma systems embedded in the cor-

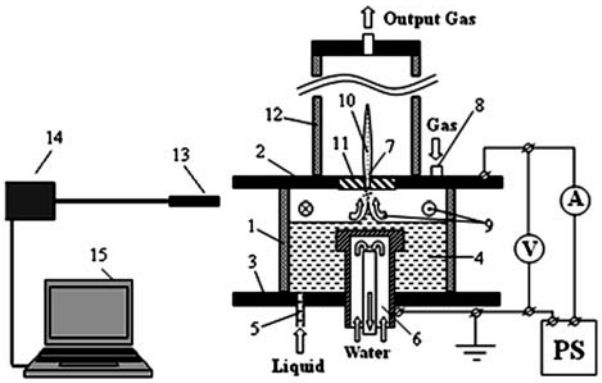

Fig. 1. Scheme of experimental setup TORNADO-LE. 1 – quartz vessel, 2, 3 – flanges, 4 – liquid, 5 – inlet pipe, 6 – water-cooled electrode, 7 – nozzle, 8 – orifice, 9 – rotating gas, 10 – plasma jet, 11 – copper hub, 12 – quartz chamber, 13 – optical fiber, 14 – spectrometer, 15 – computer, PS – power supply.

responding traditional chemical technologies. Plasma works as a catalyst for chemical reactions in such complex technologies. The plasma-supported processes reforming hydrocarbons into syn-gas and combustion of hydrocarbons are the modern examples of such an approach [6, 8]. It is obvious that the most suitable plasma generators in this case can be efficient sources of non-equilibrium plasma flows.

The properties of PLS with electric discharge in a gas reverse vortex flow TORNADO with one liquid electrode and its application to the problems of liquid hydrocarbon reforming are shown in this paper. Such discharge systems with solid electrodes are perspective non-equilibrium plasma flow generators [5]. Some attention is paid to testing the effect of electrode surface passivation in PLS.

Experimental results

Plasma-liquid system reactor was prepared with the direct current (DC) discharge in a reverse vortex gas flow of tornado type with a "liquid" electrode (TORNADO--LE) as is shown in Fig. 1. It consists of a cylindrical quartz vessel (1) of 9 cm in diameter and 5 cm in height, sealed by flanges at the top (2) and at the bottom (3). The vessel was filled with a working liquid (4) through an inlet pipe (5) and the level of liquid was controlled by a spray pump. The basic cylindrical T-shaped stainless steel water-cooled electrode (6) on the lower flange (3) made from stainless steel is fully immersed in the liquid. The electrode on the upper flange (2) made from duralumin had a special copper hub (11) with an axial nozzle (7) of 2 mm in diameter and 6 mm in length. The gas was injected into the vessel through an orifice (8) in the upper flange (2) tangentially to the cylinder wall (1) and created a reverse vortex flow of tornado type, so the rotating gas (9) went down to the liquid surface and moved to the central axis where flowed out through a nozzle (7) in the form of jet (10) into a quartz chamber (12). Since the area of minimal static pressure above the liquid surface during the vortex gas flow is located near the central axis, it creates the column of liquid at the gas-liquid interface in the form of the cone with a height of ~ 1 cm above the liquid surface (without electric discharge).

The voltage was supplied between the upper electrode (2) and the lower electrode (6) in the liquid with the help of the DC power source powered up to 10 kV. Two modes of the discharge operation were studied: the mode with "liquid" cathode (LC) and the mode with "solid" cathode (SC): "+" is on the flange (2) in the LC mode, and "–" is on the flange (2) in the SC mode. Two modes of the discharge operation were studied: the mode with "liquid" cathode (LC) and the mode with "solid" cathode (SC): "+" is on the flange (2) in the LC mode, and "–" is on the flange (2) in the SC mode.

The air flow ~ 150 cm^3/s in our system caused liquid cone creation at the center of the liquid surface. The cone height was near 5 mm and it was supported by vortex flow (Fig. 2a). In a more intensive flow (Fig. 2b), with the apex begin tear drops of the liquid, their diameter was in the range 0.5–1.0 mm. Fluid loss by increasing the air flow increases, so the frequency separation of droplets is also growing.

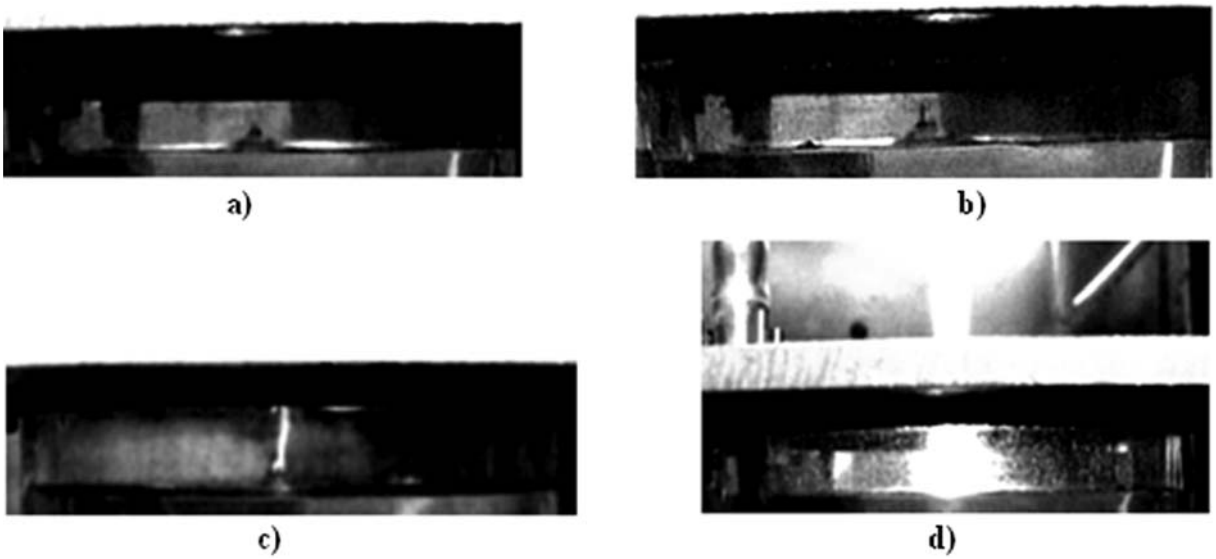

Fig. 2. Photo of experimental setup TORNADO-LE: stable water cone (air flow 110 cm^3/s, voltage-off) (a); break away of liquid drops (air flow 150 cm^3/s, voltage-off) (b); breakdown of gas gape (c); stable discharge burning (d).

The breakdown of the gas gap in the SC mode occurred at the voltage of 4.5 kV. The formation of the discharge corresponds to the classical scheme for the breakdown at atmospheric pressure in a non-uniform electric field. First comes a streamer (Fig. 2c), and after 1–2 s a stationary level (Fig. 2d).

The current-voltage characteristics of discharge in oscillating vortex flow TORNADO with liquid electrodes in different blends are presented in Fig. 3: air/H_2O (Fig. 3a); air/C_2H_5OH + H_2O (Fig. 3b); Ar/H_2O (Fig. 3c); Ar/C_2H_5OH (Fig. 3d).

When air flow to the discharge in a mixture of air/H_2O is increasing, the slope of current-voltage characteristics is changed. The voltage increases with increasing current when air flow is ~ 25 cm^3/s (Fig. 3a). The voltage does not change with increasing current when air flows ~ 55–110 cm^3/s. During the discharge in a mixture of air/C_2H_5OH + H_2O with the concentration of ethanol 4.4 mol/l (Fig. 3b) in the range of air flow 55–165 cm^3/s, the slope of current-voltage characteristics has not been changed. A similar situation is observed in a mixture of Ar/H_2O (Fig. 3c) when the gas flow is ~ 110–220 cm^3/s. With increasing argon flow during the discharge in a Ar/C_2H_5OH mixture the situation is changed (Fig. 3d). When a stream of argon is 110 cm^3/s, the voltage increases with increasing current. A stream of Ar at 165 cm^3/s voltage does not change with increasing current. When the flow is 220 cm^3/s, the voltage starts to decrease with increasing current. This indicates that there is a discharge type change.

The characteristic temperatures corresponding to the excited states of atoms (electron temperature T_e^*), and molecules (vibrational T_v^* and rotational T_r^* temperatures) in discharge plasma were determined by different methods. The electron temperature was defined along the lines of hydrogen and oxygen multiplets. Vibrational T_v^* and rotational T_r^* temperature were determined by comparing the experimentally measured emission spectra with those simulated using a SPECAIR platform.

Typical emission spectra of plasma discharge in TORNADO-LE system in different blends with the same polarity of SC are demonstrated in Fig. 4. The system parameters are: the gas flow is about 110 cm^3/s and the current is ~ 300 mA. Optic fiber was beamed in the middle of the discharge gap at a distance of 5 mm from the surface of the liquid.

The distance from the liquid surface to the upper flange is 10 mm. Typical emission spectra of plasma discharge in a mixture of air/H_2O are shown in Fig. 4. The main components in the emission spectrum is the band hydroxyl OH (A-X), atomic hydrogen line H_α (656.3 nm), H_β (486.1 nm) and oxygen multiplets O (777.2, 844.6, 926.6 nm). Emission spectrum was normalized to a maximum intensity at the wavelength λ = 283.1 nm. The metal electrode material – copper (Cu) is not observed in the plasma emission spectra. This indicates that the metal electrode material is not introduced in the plasma-liquid system TORNADO-LE discharge gap. Electron temperature T_e^*(H) = 3500 ± 500 K, T_e^*(O) = 5000 ± 500 K remained practically un-

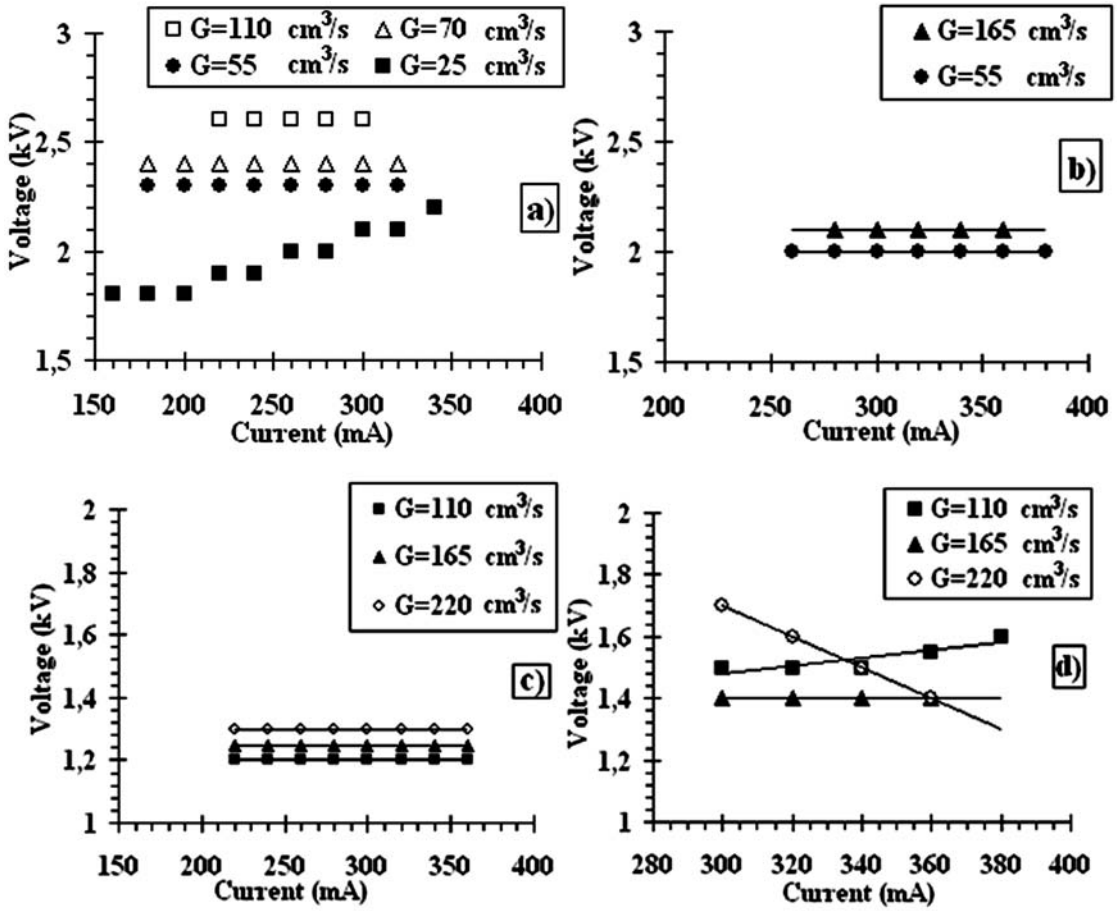

Fig. 3. Typical volt-ampere-characteristics of discharge in TORNADO-LE at regime SC: distilled water/air mixture (a); ethanol/distilled water/air mixture (b); distilled water/argon mixture (c); ethanol/argon mixture (d).

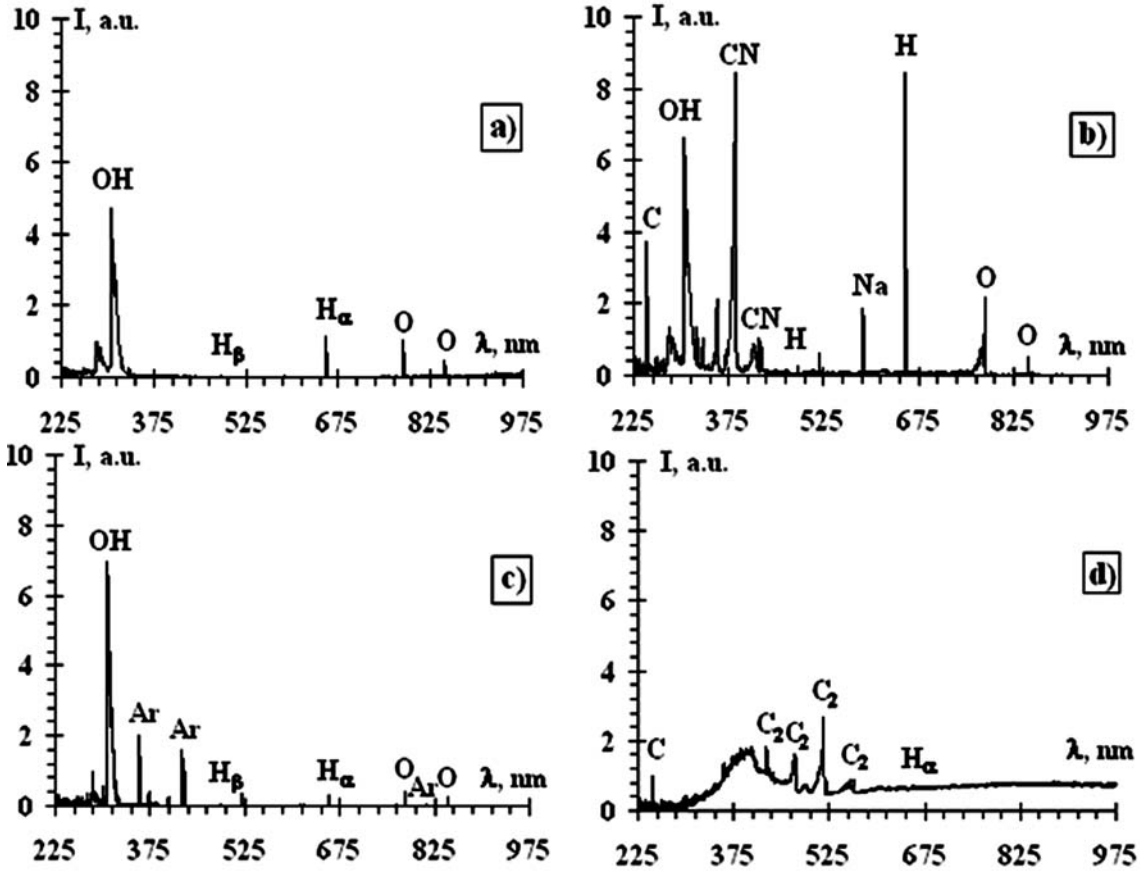

Fig. 4. Typical emission spectra of plasma in TORNADO-LE at regime SC, current 300 mA: distilled water/air mixture, voltage 2.4 kV, air flow 110 cm^3/s (a); ethanol/distilled water/air mixture, voltage 2 kV, air flow 110 cm^3/s (b); distilled water/argon mixture, voltage 1.2 kV, argon flow 110 cm^3/s (c); ethanol/argon mixture, voltage 1.4 kV, argon flow 110 cm^3/s (d).

changed and inequality $T_e^*(O) > T_e^*$ is (H) performed. Temperatures T_v^* and T_r^* are defined by hydroxyl strips OH (A-X). Rotational temperature is equal to the vibrational one in the discharge gap: T_v^* (OH) = T_r^* (OH) = 4000 ± 200 K. Rotational temperature T_r^* (OH) = 3200 ± 200 K is less than the vibrational T_v^* (OH) = 4200 ± 200 K in the plasma torch. This means that such plasma is "warm", but in non-equilibrium. Emission spectrum of plasma discharge in a mixture of air/C_2H_5OH + H_2O is shown in Fig. 4b with an ethanol concentration of ~ 4.4 mole/l. The main components in the emission spectrum are OH, C_2, CN, H, C, Na, O. Emission spectrum of plasma discharge in a mixture of Ar/H_2O is shown in Fig. 4c. Hydroxyl (OH) band and atomic lines of hydrogen H_α (656.3 nm), H_β (486.1 nm), oxygen O and Ar are attended here.

Emission spectrum of plasma discharge in a mixture Ar/C_2H_5OH is shown in Fig. 4d. It was normalized to the maximum, which is located at a wavelength of 247.8 nm. Bands of molecular carbon C_2, the line of atomic carbon C (247.8 nm) and hydrogen H_β (486.1 nm), H_α (656.3 nm) are here and part of continuous spectrum was observed also. Appearance of the latter proved the fact that soot is present in the plasma.

In the power range of 420–610 W, which was utilized in the discharge at different gas flow, the temperature of soot was actually on the same level 3400 ± 100 K. At discharge in a mixture of air/C_2H_5OH + H_2O (Fig. 4b), in contrast to Ar/C_2H_5OH (Fig. 4d), on the emission spectra bands carbon molecule C_2 are not observed. There is no continuous spectrum connected with soot.

Gas chromatography was used for the determination of component of the fabricated gas. The main components of the fuel mixture are H_2 and CO. The quantity of hydrocarbons such as C_xH_y is very small. Probably, they are destroyed under molecular hydrogen and carbon oxides formation. The dependence of the molecular hydrogen concentration on the magnitude of discharge current is measured experimentally [3] and calculated [2] (Fig. 5). The concentration of H_2 increases with increasing current in the experiment. The calculation shows that H_2 concentration saturates under operating currents.

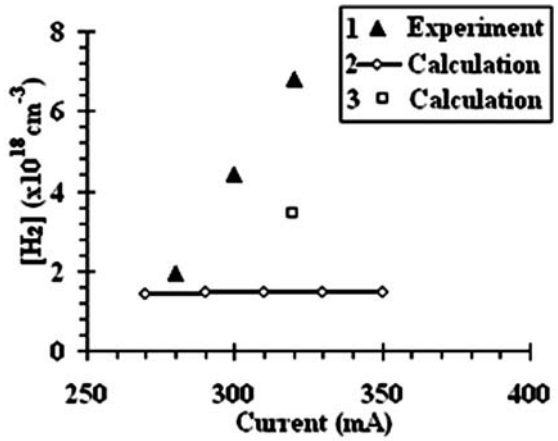

Fig. 5. Synthesis gas yield depends on the magnitude of current in the discharge: experiment at ethanol concentration 4.4 mole/l (1); calculation at ethanol concentrations 1.1 mole/l (2) and 2.2 mole/l (3).

A comparison of the plasma emission spectra from discharge with a positive electrode embedded in water showed a difference. The latter was connected with electrode material. When such an electrode was produced from stainless steel (SLS), the electrode material lines are absent in the spectrum. But they are present in the case of copper electrode. At the same time, simulating the plasma emission spectra of these materials demonstrates the comparability of their maximum intensity lines at wavelengths 324 nm (Cu) and 358 nm (SLS).

At the same time, simulating the plasma emission spectra of these materials demonstrates the comparability of their maximum intensity lines at wavelengths 324 nm (Cu) and 358 nm (SLS). A rapid (~ 1 min) transformation of colorless water into dark brown one was observed with a copper anode immersed in water. The water with SLS anode remained clear. All these phenomena are based on the known features of the electrochemical processes in copper and iron compounds [1]. So, it proves the validity of the metal electrode surface passivation phenomenon in plasma-liquid systems.

Summary and conclusions

- The plasma of TORNADO-LE discharge is "warm" weak non-equilibrium plasma.
- The main components of the synthesis gas produced from ethanol in the PLS – TORNADO-LE reactor are molecular hydrogen H_2 and carbon monoxide CO, whose relative yield is many times higher than that for hydrocarbons CH_4, C_2H_2, C_2H_4, and C_2H_6.
- The composition content of synthesis gas and the power inputs on the ethanol conversion in the TORNADO-LE discharge depends on the initial gas that forms the plasma and on the ethanol-water ratio in the solution.
- The kinetic plasma-chemical modeling is in fairly good agreement with the experimental data, at least, for the main synthesis gas components, H_2 and CO, predicting a non-thermal plasma-chemical mechanism of the ethanol conversion in the investigated plasma-liquid system.

The existence of electrochemical passivation phenomenon on the positive electrode surface in the plasma-liquid system is demonstrated.

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