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PLASMA-LIQUID SYSTEM WITH REVERSE VORTEX FLOW FOR PLASMA-CATALYTIC REFORMING

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A plasma-liquid system with the reverse vortex flow and a liquid electrode, which was designed for the plasma-catalytic reforming of hydrocarbons, has been studied. Discharge operation modes with the solid and liquid cathodes are compared, including the discharge voltage dependences on the distance between the upper flange and the liquid surface. The influence of the water content in a plasma-forming gas on the average energy of plasma electrons is analyzed.

Keywords: plasma-liquid system, plasma-catalytic reforming, reverse vortex flow, liquid electrode.

1. Introduction

Numerous researches that were aimed at the development of new alternative energy sources stimulated the growth of interest to new applications of plasma chemistry in power engineering. Plasma is an excellent source of active particles, and it can be used to improve the efficiency of various industrial chemical technologies [1]. Of special interest is the development of technologies for reforming hydrocarbons into hydrogen or synthesis gas with the use of plasma [2]. Those technologies may initiate an active introduction of such renewable hydrocarbons as biofuel into chemical, power, and transport industries.

Previous researches definitely testify that the straightforward application of isothermal plasma for reforming hydrocarbons is inefficient in comparison with the application of non-isothermal plasma [3] and the plasma-catalytic approach [4] to hydrocarbon reforming. In order to satisfy the requirements that would open a way for the plasma-catalytic reform-

ing to commercialization, the discharge system that is used in a reforming installation must be capable of generating the non-equilibrium (non-isothermal) plasma at the atmospheric pressure and effectively introducing it into a reforming chamber. The largest obstacle for the wide implementation of plasma-catalytic technologies is the short term of a continuous work of ordinary plasma generators.

To overcome the restrictions inherent to traditional plasma sources, plasma-liquid systems [5] on the basis of rotating gliding discharges can be used. The latter combine the ability of gliding discharges to generate non-equilibrium plasma at the atmospheric pressure [6] and a possibility to substantially prolong the service life of a discharge system due to the gliding of a discharge channel along the surface of electrodes in the course of its rotation under the influence of a gas flow. The operating time of the discharge system increases additionally, because one of its electrodes is covered with liquid and, in effect, forms a liquid electrode. The main advantage of liquid electrodes is their capability to maintain a stable level of liquid and, therefore, prevent the electrode de-

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struction and maintain stable values of discharge parameters. Furthermore, the composition of generated plasma strongly depends on the composition of liquid; this circumstance creates new ways to control parameters for plasma sources of this type.

The efficiency of the plasma-catalytic system for reforming hydrocarbons directly depends on the volume occupied by the plasma torch in the reaction chamber. To provide the maximum plasma volume, the optimum way is to inject plasma in the form of plasma torch, which is suitable for the use in plasma-catalytic systems and provides a design with a high scaling ability. In order to obtain the maximum control over the plasma torch injection, the torch has to be stabilized. Stability of high-pressure discharges in powerful plasmotrons is reached, as a rule, by introducing a vortex gas flow [7]. The introduction of a reverse vortex gas flow of the “tornado” type into the plasma-liquid system ensures both formation and stabilization of a plasma torch [8].

2. Experimental Installation and Methods

A schematic diagram of the experimental installation is shown in Fig. 1. The installation was constructed on the basis of a plasma-liquid system with liquid electrode. The reforming system included a discharge and a reaction chamber. The discharge system consisted of a cylindrical quartz chamber, which was closed from both its sides by stainless steel flanges. T-shaped cylindrical electrode (1) was mounted at the center of the lower flange. The upper flange had an aperture, in which copper plug (3) was fixed. The quartz chamber was filled with distilled water (2), which completely covered the lower metal electrode. The required level of liquid in the chamber was maintained by supplying water into the chamber through an input aperture in the lower flange with the use of a syringe pump. Gas was let into the system through input apertures (5) located in the upper flange. The gas flow was directed along the tangent to the wall of a quartz chamber, which gave rise to the formation of a vortex gas flow moving along the water surface to the quartz cylinder axis and leaving the discharge chamber through the aperture in the upper flange.

One of the ends of the discharge-generated plasma channel was connected with the copper plug surface, and the other end with the liquid surface. The reverse

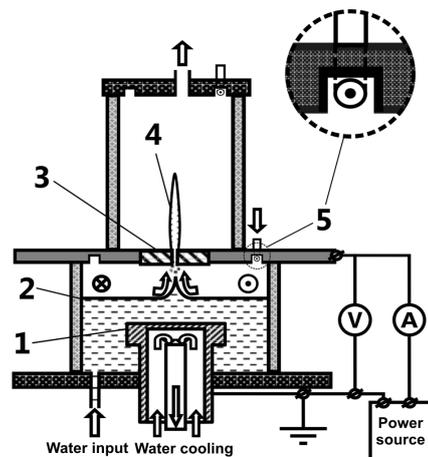


Fig. 1. Schematic diagram of the experimental installation for the plasma-catalytic reforming

vortex gas flow invoked the plasma channel to rotate around the axis of the system and to exit from the aperture in the copper plug in the form of a plasma torch (4). The plasma channel end that was located at the solid electrode glided along the copper plug surface at the rotation. The potential difference between the electrodes was created with the use of a dc power source, which could supply a voltage of up to 7 kV.

The discharge had two operating modes, which could be chosen by selecting the position of the cathode in the discharge system. Namely, it was the lower electrode in the liquid cathode (LC) mode, and the upper electrode in the solid cathode (SC) one. During the experiment, the anode was grounded, and a high voltage was supplied to the cathode.

The behavior of a discharge in various operating modes was recorded on a videocamera to be analyzed visually. The required discharge parameters were obtained by analyzing the corresponding current-voltage characteristics. The obtained data were used to study the dependences of discharge parameters on the distance between the solid and liquid electrodes. Plasma diagnostics was carried out with the help of optical emission spectroscopy.

The emission spectra were registered, by using a spectral device consisting of an optical fiber and a calibrated spectrometer Solar TII S-150-2-3648 USB. The device allowed spectral lines to be registered in a wavelength interval from 200 to 1000 nm with a resolution of less than 0.13 nm/pixel. The electron tem-

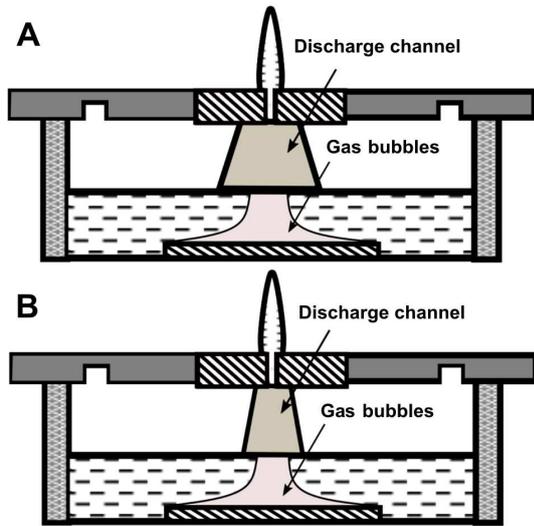


Fig. 2. Schematic diagram of the discharge system: the LC mode (A), the SC mode (B)

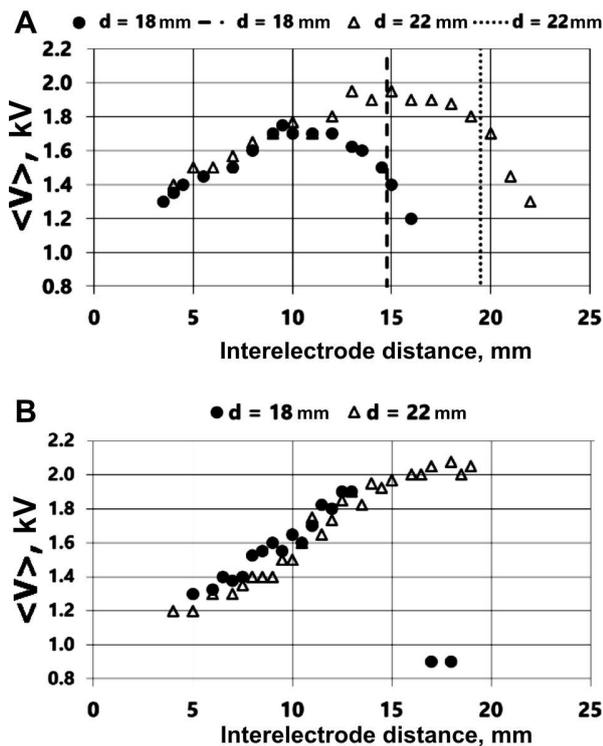


Fig. 3. Dependence of the discharge voltage on the distance between the upper flange and the liquid surface: the SC mode (A), where lines mark the points, at which the discharge changes its type; the LC mode (B). d is the distance between the upper flange and the cylindrical T-shaped electrode imbedded into liquid. The current equals 340 mA

perature T_e^* of atomic hydrogen H was determined by analyzing the relative integrated intensities of spectral lines H_α (656.3 nm) and H_β (486.1 nm). The electron temperature of atomic oxygen was calculated with the help of Boltzmann diagrams and with the use of three most intense multiplets of atomic oxygen (at 777.2, 844.6, and 926.6 nm). The rotational, T_r^* , and vibrational, T_v^* , temperatures of hydroxyl (OH) and nitrogen (N_2) were determined, by comparing the experimental emission spectra of plasma with the spectra calculated with the help of software code SPECAIR [9] and with the use of the electron temperature of atomic oxygen (O) obtained with the help of Boltzmann diagrams.

3. Results and Their Discussion

The analysis of the video recorded during the experiment showed that the discharge channel has a larger diameter in the LC mode than in the SC one. In Fig. 2, the behaviors of a discharge in two operating modes are compared. The discharge channel diameter amounted to 7.4 ± 0.5 mm in the SC mode and 12.8 ± 0.5 mm in the LC one.

Depending on the operating mode, the gas generated in a liquid owing to its electrolysis had different compositions. It was hydrogen in the LC case, and oxygen in the SC one. The presence of a discharge channel reduced the surface tension of water and invoked an intense bubbling through the interaction interface between plasma and liquid. It is worth to note that the width of the channel, along which the gas bubbles move, decreases nonlinearly starting from the surface of the lower solid electrode (Fig. 2). At a certain distance, the width of the channel with gas bubbles acquires a constant width.

The current-voltage characteristics of the discharge were measured at distances of 18, 22, and 27 mm between the upper and lower solid electrodes. The measurements were carried out after the liquid surface had been stabilized at the interface of its interaction with the discharge channel. The corresponding experimental data on the current-voltage characteristics can be found in work [10]. The interelectrode gap (the distance between the solid and liquid electrodes) was varied during the experiment from the minimum observable value (3 mm) to the distance between the solid electrodes. In Fig. 3, the dependence of the discharge voltage on the interelectrode

gap width is shown for two distances between the solid electrodes: 18 and 22 mm.

The discharge behaviors are quite different in the SC and LC modes. In the former case, the voltage dependence on the gap width is nonmonotonic: at first, it pronouncedly grows; then it has a short stable section, which afterward transforms into a drastic voltage drop. The voltage growth at the initial stage can be a result of the interelectrode distance growth and the introduction of oxygen, which is formed in the liquid at electrolysis, into the discharge channel. Oxygen is an electronegative gas, and, when getting into the discharge channel, it increases the voltage required to maintain the discharge. Since an increase of the interelectrode distance corresponds to a reduction of the liquid layer thickness, there is a time moment, when the width of the channel filled with oxygen bubbles exceeds the width of the discharge channel. As a result, the amount of oxygen in the discharge channel decreases, and its influence on the discharge becomes weaker, which reduces the voltage magnitude required to maintain the discharge. When the water layer reaches a certain minimum thickness, the discharge channel pushes the liquid aside and gets fixed at the surface of the lower solid electrode. Accordingly, the discharge system passes to the mode with two solid electrodes and a fixed interelectrode distance. This transition leads to a reduction in the discharge gap resistance and diminishes the voltage drop across the water layer. This explanation is supported by a change in the discharge behavior, which was registered during the visual analysis of the video obtained for the process under study. The points of transition from the discharge with a liquid electrode to the discharge with solid electrodes are marked in Fig. 3 by vertical dashed lines.

The dependence of the discharge voltage on the interelectrode distance in the LC mode monotonically increases. Due to a larger contact area between the discharge channel and the water surface in the LC mode, we may assume that the amount of hydrogen that gets into the discharge channel does not become smaller, as the interelectrode distance grows. Accordingly, the voltage dependence on the interelectrode distance corresponds to the same behavior of the discharge system as was observed at the stage of initial voltage growth in the SC mode. For an interelectrode distance to be 18 mm, the liquid layer reaches the critical minimum, and the discharge changes to the

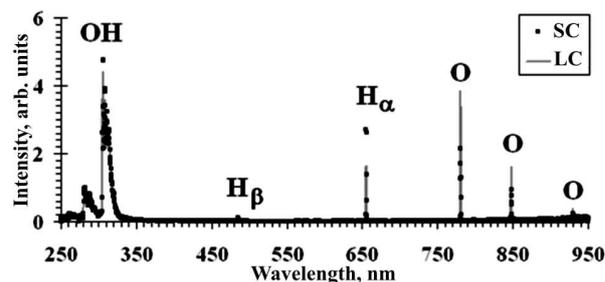


Fig. 4. Emission spectra of discharge plasma in the SC and LC operating modes

electric arc mode, which results in a drastic decrease of the discharge voltage. In the case where the distance between the electrodes equals 22 mm, the discharge dies away before the thickness of the liquid layer reaches the critical value. So that the transition to the electric arc regime is not observed in this mode.

According to the plasma emission spectra (Fig. 4), the main active plasma components are OH, H, and O. The bands of N_2 are observable due to its high content in air used as a working gas. The spectra are free of bands corresponding to the products of reactions with the participation of nitrogen. In particular, there are no nitrogen oxides NO_X . This fact takes place, because the concentration of particles with energies that are high enough to dissociate nitrogen molecules (9.82 eV) is low under the experimental conditions considered in this research. For this reason, we assume that nitrogen does not participate in any chemical reaction that runs in plasma. The emission spectra of discharge plasma do not contain traces of the metal electrode materials. This fact can testify to a low level of electrode destruction and the absence of anode dissolution. The described results confirm the prediction about the potentially longer operation time for electrodes in plasma systems with a liquid electrode in comparison with systems that contain only solid electrodes.

The emission spectra were used to determine the electron temperatures T_e^* of atomic hydrogen and oxygen, as well as the rotational, T_r^* , and vibrational, T_v^* , temperatures of hydroxyl (OH) and nitrogen (N_2). For plasma in the discharge gap, the rotational and vibrational temperatures of OH have the same value, 4000 ± 200 K. This coincidence probably occurs, because the gas flow near the water surface is directed in parallel to the discharge channel and along the electric current direction. At the same time, the

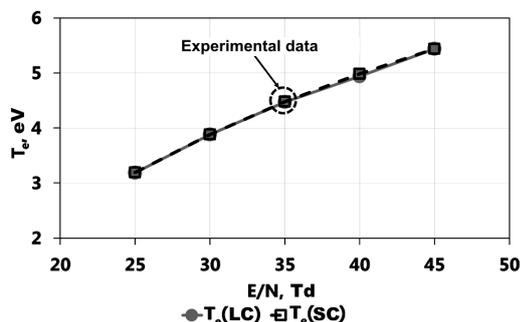


Fig. 5. Dependence of the average energy of electrons in plasma on the reduced electric field

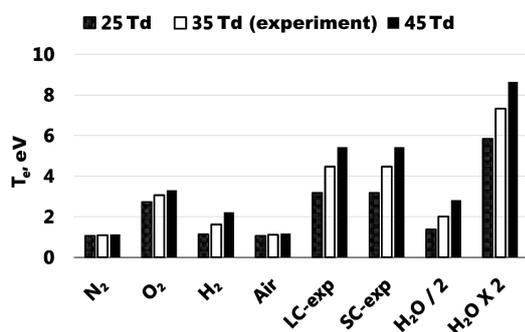


Fig. 6. Dependence of the average energy of electrons in plasma on the composition of a plasma-forming gas and the reduced electric field in the discharge

electron temperatures of H and O atoms in the discharge gap do not coincide: $T_e^*(H) = 3200 \pm 500$ K and $T_e^*(O) = 5000 \pm 500$ K. Plasma in the torch becomes non-isothermal right after its exit from the discharge gap. At a distance of 5 mm above the upper flange, the vibrational temperatures amount to $T_v^*(OH) = 4200 \pm 200$ K and $T_v^*(N_2) = 5000 \pm 200$ K, and the rotational ones to $T_r^*(OH) = 3200 \pm 200$ K and $T_r^*(N_2) = 3500 \pm 200$ K. The temperature difference can be associated with the appearance of a component of the gas flow that is directed across the plasma channel. The electron temperatures of atomic plasma components amount to $T_e^*(H) = 3500 \pm 500$ K and $T_e^*(O) = 5200 \pm 500$ K, and this difference demands for the additional research. The obtained plasma torch was introduced into the reaction chamber to a depth of approximately 150 mm.

The dependence of the discharge voltage on the interelectrode distance is used to calculate the electric field in the discharge gap, when the current was equal to 340 mA. In the case of LC mode, the whole dependence can be used. On the other hand, in the case of

SC mode, only the section of initial growth is suitable for calculations.

While calculating the average energy of electrons in plasma, which is one of the key parameters governing the chemical reaction processes, the software code BOLSIG+ (version 06/2013) [11] was used (the database of cross-sections was downloaded from the site www.lxcat.net in June 2013). In order to carry out the required calculations, some approximations were applied, which were united into a physical model. The translational temperature of plasma was put equal to the rotational temperature (4000 K) on the basis of the data obtained from the plasma emission spectra. The pressure was selected at a level of 1 atm, and the electric field at a level of 70 V/mm, which was obtained during the experiment. The composition of model gas was chosen according to the assumption that the entire introduced air interacts with the discharge, and all water losses take place due to the water evaporation from its surface at the interface of water contact with the discharge channel. The calculated values of electron temperatures in plasma and their dependences on the reduced electric field are exhibited in Fig. 5.

Figure 5 distinctly demonstrates that if the discharge current is the same, the operating mode has no effect on the average energy of electrons in the plasma of a rotating gliding discharge with a reverse vortex flow of air of the “tornado” type and a liquid electrode. Additionally, we calculated the average energies of plasma electrons for various compositions of a plasma-forming gas such as, N₂, O₂, H₂, air, water-air mixtures (in both operating modes, LC-exp and SC-exp, and taking the products of water electrolysis into account), and an experimental mixture in the LC mode with twice as low (H₂O/2) and twice as high (H₂O × 2) water contents. The average energies of plasma electrons calculated for the indicated plasma-forming mixtures and various magnitudes of the reduced electric field (25, 35, and 45 Td) are shown in Fig. 6.

The obtained plot clearly testifies that if the plasma-forming gas is nitrogen or air (nitrogen content in air approximately equals 80%), the variation of the reduced electric field weakly affects the average energy of electrons in plasma. The difference between the average energies of electrons for the experimental mixtures of gases at various operating modes is small in comparison with the calculation error for

the average electron energy. The presence of water vapor in the gas mixture gives rise to large mismatches between the average energies of plasma electrons obtained for different values of reduced electric field. The higher the water content in the mixture, the higher is the average energy of electrons in plasma.

From the analysis of the data obtained, we may assume that there is a way to control the average energy of electrons in plasma by varying the water content in a plasma-forming gas. Taking into account that the energy of plasma electrons is one of the main factors that govern the generation of specific active particles in plasma, the control over the water content in a plasma-forming gas can become an additional mechanism to drive the process of chemical transformations in the reaction chamber.

4. Conclusions

A plasma-liquid system with the reverse vortex gas flow and a liquid electrode has been developed. The plasma in the torch is non-isothermal and consists of such active components as OH, O, and H, which initiate chemical transformations. The length of the stabilized plasma torch is sufficient for the efficient injection of plasma into the volume of a chemical reactor.

Our researches have shown that the presence of water vapor in plasma-forming mixtures strongly affects the average energy of electrons in plasma, and the higher relative concentration of water results in the higher average electron energy. This fact can be used as an additional mechanism to control the average energy of electrons in plasma and, accordingly, to govern the generation of active particles in plasma, which are required to catalyze a definite chemical process.

The gas formed during the water electrolysis is found to modify the discharge parameters. Its introduction into the discharge channel gives rise to the growth of the potential difference between the electrodes at a fixed discharge current.

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 ПЛАЗМОВО-РІДІННА СИСТЕМА
 ЗІ ЗВОРОТНИМ ВИХРОВИМ ПОТОКОМ
 ДЛЯ ПЛАЗМОВО-КАТАЛІТИЧНОГО
 РЕФОРМУВАННЯ

Резюме

Досліджено плазово-рідинну систему зі зворотним вихровим потоком газу та рідким електродом, яка була розроблена для плазово-каталітичного реформування вуглеводнів. Проведено порівняння між режимами роботи розряду з твердим катодом та з рідким катодом, включаючи порівняння залежностей розрядної напруги від відстані між верхнім фланцем та поверхнею рідини. Досліджено вплив вмісту води у плазмотвірному газі на середню енергію електронів плазми.