ETHANOL CONVERSION IN GLOW AND BARRIER DISCHARGES

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The efficiency of ethanol conversion in glow and barrier discharges is analyzed. It is found that for a given power the ethanol conversion is more efficient in glow discharge. This is caused by the principal difference in the way of generation of active atoms and radicals in both types of discharges. In addition, the main channels leading to the generation and quenching of H_2 and CO are studied. The method to increase the efficiency is proposed.

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INTRODUCTION

Nowadays, mixture of molecular hydrogen H_2 and carbon monoxide CO (further, syn-gas) is used for the synthesis of different chemicals [1], is used as an intermediate reagent for the liquid fuel generation [2] as well as it is proposed using as an alternative fuel [3].

One of the efficient ways of syn-gas production is its generation from the ethanol in non-equilibrium plasmas of electrical discharges in plasma-chemical reactors of different types [3, 4]. The choice of non-equilibrium plasma is caused by more efficient use of electrical power [4-6]. The main types of discharges for the generation of non-equilibrium plasma are glow discharge (GD), dielectric barrier discharge (DBD), high-frequency and microwave discharges. Both GD and DBD are widely used discharges for the generation of syn-gas. For instance, DBD was studied experimentally in [7], while GD was studied in [8]. The comparison between these two papers shows that for the same power GD allows obtaining larger density of syn-gas. Also, in accordance with [4] DBD has smaller energy efficiency in comparison with other discharges. The difference between these discharges requires detailed study.

The aim of the present paper is the comparison of efficiency of the ethanol conversion in DBD and GD. For this purpose the global (zero-dimensional) model is used. It is assumed in this model that the initial component content of the gas mixture is identical for both discharges. Also, the power introduced in the discharge is also assumed to be the same.

1. PHYSICAL MODEL

In order to study the plasma kinetics in both discharges the model developed in [10] is used. The gas mixture consists of argon (typical density $\sim 10^{19}$ cm^{-3}), ethanol ($\sim 10^{18}$ cm^{-3}) and water ($\sim 10^{18}$ cm^{-3}). Argon is used as a buffer gas. Its admixture increases the average electron energy, which results in the increase in the rates of electron-molecular reactions. In addition, since argon is a rare gas it does not participate in chemical reactions. This simplifies the analysis of the obtained results.

It is assumed that DBD is the sequence of discharges which temporal duration is 15 ns (power-on stage). At this stage one obtains the electric current through the cathode-anode gap. These discharges are separated by the intervals when the power is turned off (power-off stage). The frequency of discharges is 18 kHz. In the opposite, in GD the power is introduced in the discharge continuously. In order to compare DBD and GD the calculations are carried out for the time during which the same energy is spent.

The following assumptions are made in the model: 1) electrical power introduced in the discharge is averaged over the entire discharge volume; 2) electric field in the discharge is homogeneous and is constant in time; 3) discharge plasma column is homogeneous; 4) temperature of the gas mixture is constant and equal to 400 K. Such choice of the gas temperature is caused by the fact that usually ethanol is converted in overheated mixture. The gas pressure is atmospheric.

2. NUMERICAL MODEL

Numerical modeling includes the following steps: 1) calculation of the electron energy distribution function (EEDF) with the accounting for elastic and non-elastic electron-neutral collisions (with argon, ethanol and water); 2) numerical solution of the system of kinetic equations in zero-dimensional approximation. Kinetic mechanism includes 30 species (C_2H_5OH, O_2, H_2O, H_2, CO, CH_4, CH_3CHO *etc*), 43 electron-molecular reactions and 130 chemical reactions. The rate coefficients of latter processes are taken from NIST database (for details see [10]).

The following system of kinetic equations is solved numerically:

$$\frac{dN_i}{dt} = \sum_j k_{ij} N_i N_j + \sum_{j,l} k_{ijl} N_i N_j N_l + S_{ei}. \quad (1)$$

Here N_i, N_j, N_l are the densities of molecules and radicals, k_{ij}, k_{ijl} are the rate coefficients of chemical reactions for i^{th} component of gas mixture, and S_{ei} are the rates of electron-molecular reactions. The method to define S_{ei} as well as the list of these reactions is detailed in [10]. In GD S_{ei} are calculated at each time step, while in DBD they are calculated only during the power-on stage. Otherwise, S_{ei} are assumed equal to zero.

3. RESULTS

The simulation results have shown that in both discharges the main channel of H_2 generation is the reaction between ethanol and hydrogen atoms:

$$C_2H_5OH + H \rightarrow C_2H_5O + H_2. \quad (2)$$

However, as it is shown in Fig. 1, the density of H_2 is 4 orders of magnitude larger in GD than in DBD. This indicates on the larger efficiency of GD.

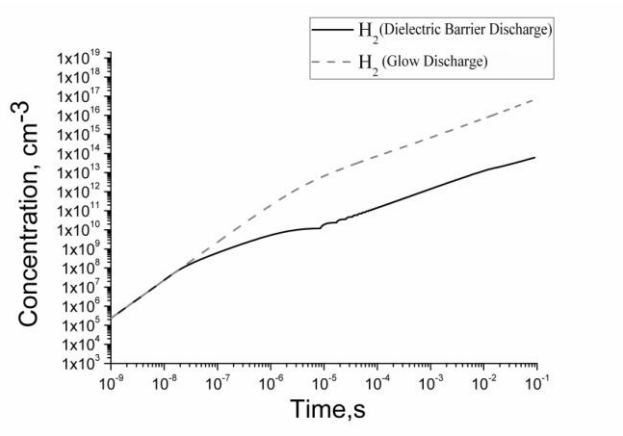

Fig. 1. Temporal evolution of the H_2 density in glow and dielectric barrier discharges

The variation of ethanol density during the simulations can be neglected in comparison with the variation of densities of active species. Therefore, in further analysis the density of C_2H_5OH is assumed constant. Keeping constant the ethanol density in reaction (2) one concludes that the difference in efficiency of DBD and GD is explained by the different dynamics of H density in both discharges. The latter is caused by the different temporal duration of reaction of H generation. The simulation results have shown that during the discharge the main reaction of H generation is the ethanol dissociation by the electron impact:

$$C_2H_5OH + e \rightarrow C_2H_5O + H + e. \quad (3)$$

In DBD this reaction works only during 15 ns, i.e. during the power-on stage. Between subsequent discharges the mixture is not affected by the discharge. Since the gas temperature is small the rate coefficients of thermo-dissociation reactions are small. Therefore, active species are not generated during the power-off stage. These species very fast (during a few microseconds) recombine generating stable molecules (Fig. 2). Figs. 2,a,b show the comparison between the time evolution of H density in GD and DBD. One can see that in GD the density of H grows during ≈1 μs until it reaches the saturation level (~10^{13} cm^{-3}).

Fig. 1 shows that at this stage the density of H_2 also grows. Since the time duration of one current pulse in DBD is only 15 ns, the power is turned off before the density of H reaches the steady-state value. It reaches much smaller value of ~10^{10} cm^{-3}. This results in the substantial difference between rates of reaction (2) obtained in DBD and GD. As a consequence, one obtains different efficiency of syn-gas generation in these discharges. In addition, one can conclude from Fig. 2 that in DBD each consequent discharge acts on the mixture which is free from active species. That is, reaction (2) starts with some time delay.

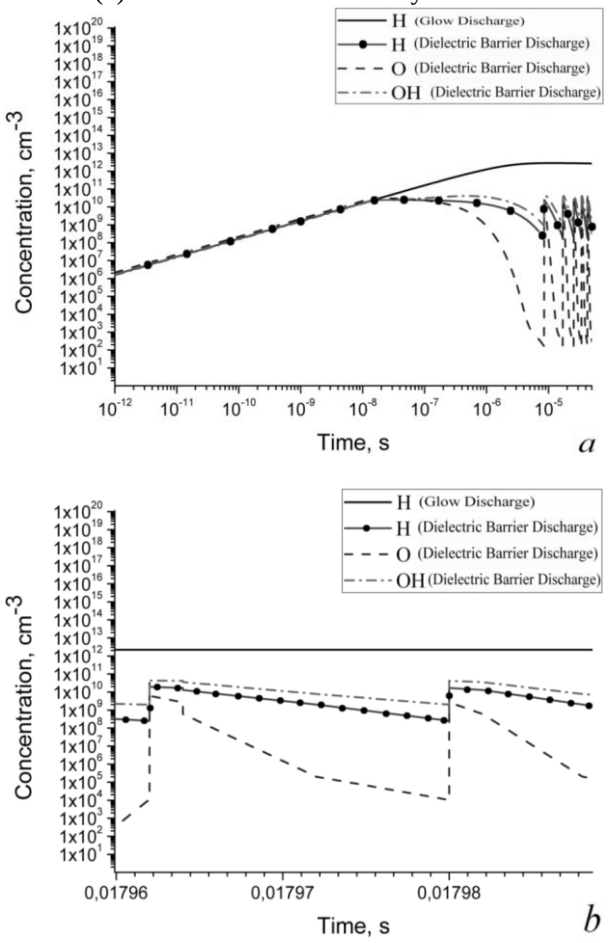

Fig. 2. Temporal evolution of the densities of H, O and OH (a) in the initial moment of time, and (b) at later times

Another important component of syn-gas is the carbon monoxide CO. Fig. 3 shows its temporal evolution obtained for both discharges.

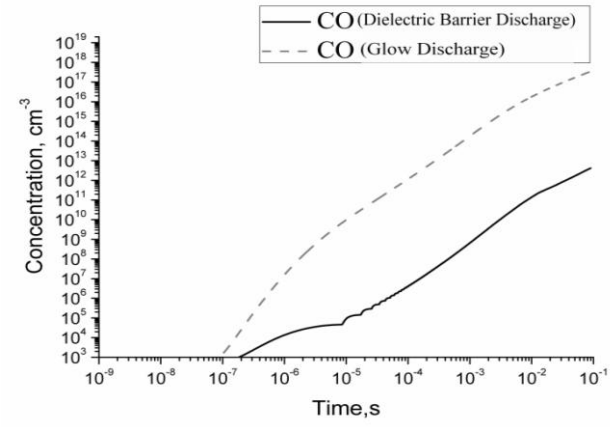

Fig. 3. Temporal evolution of the CO density in glow and dielectric barrier discharges

One can see that again the efficiency of CO generation is higher in GD. Analysis of the plasma kinetics has shown that CO is mainly generated in the following reactions:

$$CH_3CO + M \rightarrow CH_3 + CO + M, \quad (4)$$

$$HCO + O_2 \rightarrow CO + HO_2, \quad (5)$$

where M is the third body (in the present model it is H_2O or C_2H_5OH). Radicals CH_3CO and HCO are generated efficiently only during the discharge (or the power-on stage of DBD). During the power-off stage these radicals are quenched. Thus, in analogy with H_2, the difference in efficiency of CO generation in DBD and GD is explained by different ways of power introduction in the discharge.

CONCLUSIONS

Thus, one can conclude that the ethanol conversion in DBD occurs only during short current pulses having temporal duration of 15 ns. As a consequence, the efficiency of ethanol conversion is higher in GD than in DBD for the same initial conditions and the same power introduced in the discharge. From this point of view the use of GD for the generation of H_2/CO mixture is more profitable. This result is in qualitative agreement with the results presented in [7, 8].

The disadvantage of pulsed discharge can be removed by the increase in the frequency of discharge pulses. As was obtained above, the main channel of H quenching is the reaction (2), which leads to the generation of H_2. The rate coefficient of this reaction at gas temperature of 400 K is $\approx 2.4\times10^{-14}$ $cm^{-3}\cdot s^{-1}$. Assuming that the largest density of H in DBD is $\approx 2\times10^{10}$ cm^{-3} one estimates the rate of (2) as $\approx 7\times10^{15}$ cm^3s^{-1}. The estimation of time during which the density of H decreases by the order of magnitude gives ≈1 μs. Thus, it is possible to increase the efficiency of ethanol conversion in DBD, if one increases the frequency of the pulses up to 1 MHz. This will occur because each subsequent discharge will act on the mixture containing enough active atoms and radicals. However, the majority of dielectrics are damaged at high frequency due to capacitive currents. Therefore, it seems promising to replace DBD by high-frequency and microwave discharges. For these discharges the frequency 1 MHz and higher is standard. Moreover, for these discharges high frequencies are supported easily at atmospheric pressure. In the opposite, different instabilities develop in glow discharges at these conditions.

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КОНВЕРСИЯ ЭТАНОЛА В ТЛЕЮЩЕМ И БАРЬЕРНОМ РАЗРЯДАХ

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Анализируется эффективность преобразования этанола в тлеющем и барьерном разрядах. Обнаружено, что при заданной мощности преобразование этанола является более эффективным в тлеющем разряде. Это обусловлено различием в способе генерации активных атомов и радикалов в обоих типах разрядов. Также изучаются основные каналы, ведущие к генерации и тушению молекул H_2 и CO. Предложен способ по повышению эффективности конверсии этанола в барьерном разряде.

КОНВЕРСІЯ ЕТАНОЛУ У ТЛІЮЧОМУ ТА БАР'ЄРНОМ РОЗРЯДАХ

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Аналізується ефективність перетворення етанолу в тліючому і бар'єрному розрядах. Виявлено, що при заданій потужності перетворення етанолу є ефективнішим у тліючому розряді. Це обумовлено розходженням у способі генерації активних атомів і радикалів в обох типах розрядів. Також, вивчаються основні канали, що ведуть до генерації та гасіння молекул H_2 і CO. Пропонується спосіб щодо підвищення ефективності конверсії етанолу в бар'єрному розряді.