LOW TEMPERATURE PLASMA AND PLASMA TECHNOLOGIES

PLASMA CATALYSIS OF CHEMICAL REACTIONS

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The features of the ethanol reforming with the influence of exothermic chemical reactions on the level of non-equilibrium gas-discharge plasma are discussed. It is shown that effect of chemical reactions on the level of non-isothermality plasma itself can be extremely high and aimed at reducing the difference between translational and vibrational temperatures of plasma. The coefficient of transformation of electric energy into the chemical energy of the produced syngas has substantial increase when plasma activation of the fuel mixture of both components is transited to the activation of the oxidizer only in the hybrid plasma-catalysis partially-oxidation reformer system.

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INTRODUCTION

It is known that plasma generation is associated with the usage of the most expensive form of energy, namely - the electrical energy. Its production consumes three times more chemical energy. Therefore, the power input is require a special attention during the introduction plasma technologies into the manufacturing. Such energetic parameters as: the energy cost of the desired product, energy efficiency, scalability, etc. are used today as indicators of efficiency for any plasma chemical technology characterization. Obviously, the absolute values of these variables can vary over a wide range for the same plasmachemical system.

Thus, power inputs are depended essentially on the reactant concentration in the initial solution under destruction of organic substances in the plasma-liquid systems (PLS). For example, during the phenol degradation in the plasma-liquid DC system with the secondary discharge supported by the transverse arc the linear growth of the energy efficiency of the initial solution concentration was observed in all studies for the concentration range of $10^{-1}$–$0.5$ M, and the energy of the destruction varied appropriately in the range of $10^4$–$10^5$ eV/molecule [1].

Similar results were obtained for the degradation of surfactant $(C_6H_{29}NC_2H_5Br)$ and DDT (dihlurdifenirhirotean) in this DC PLS [2].

It should also be noted that efficiency of the known techniques with using high-power plasma torches is of the same order. So the mixture, consisting of 68% beryllium oxide and 32% petroleum coke, is chlorinated during producing beryllium chlorides from the beryllium oxide with using of the plasma electric arc setting [3]. Chlorine was added into the plasma-forming gas (nitrogen). The final product contains 98% BeCl₂ and 2% initial unreacted material. A number of impurities in Be after cleaning does not exceed 0.1% according to spectral analysis data. Conversion of the beryllium oxide into the chloride by this technology is 67% with specific energy consumption 115 kW•h (2.6•$10^{-7}$ eV) per 1 kg of reagent $(7.8•10^{21}$ BeCl₂ molecules), i.e. 330 eV per molecule.

Obviously, the reduction of energy consumption for the destination product is connected with the selective plasma chemical transformation. It is known that achievement of the high selectivity of chemical reactions and purity of outlet products in plasma chemical systems is possible with usage of non-equilibrium ”cold” plasma. A high level of electron energy and concentrations of excited and charged particles at the low gas temperature is specific characteristics of such plasma [4].

Today we have a large number of modern plasma studies, which are devoted on chemical transformations of substances in the non-equilibrium plasma of electric discharges [5]. The main goal of the most of these investigations is to examine the products and regularities of its formation in order to develop technologies of creation a new substances and materials with interesting features and modification the existed substances and materials.

Quantitative measurements of the internal plasma parameters (such as: the electric fields distribution in plasma, concentration and electron energy distribution functions (DF), heavy particles temperature, particles DF on internal excitation levels, especially on the vibration and electronic levels, the radical concentrations), which affect the rate and kinetics of processes in plasma systems, are usually not carried out. In the case when such measurements have been performed it is often that measured parameters are not enough make detailed analysis of the possible mechanisms of plasma processes. High rates of plasma-chemical reactions results from the high concentration of excited atoms and molecules in electric discharges as a rule. At the same time, the physical and chemical processes in quasi-equilibrium and non-equilibrium plasmas are multi-channel. It is connected with the fact that they pass through a large number of vibrational or electron-vibrational levels with formation of excited states and excited intermediate products in different quantum states. Such multichannel nature of physico-chemical processes in the presence of deviations from thermodynamic equilibrium leads to the fact that the direct and inverse processes are often pass through different quantum states.
So, the question remains: how to change the level of the non-equilibrium state in plasma systems when reactive components are injected in it. We believe that a great importance should have in the case of exothermic processes. This paper investigates some aspects of this problem.

1. ENERGETICS OF CHEMICAL REACTIONS

Traditionally [6] introduced the concept of the reaction path when considering the energy of chemical reactions. So the way reaction of exchange (A + BC \(\rightarrow\) AB + C) there is a line in the configuration space, which corresponds to the minimum energy of the interaction of atoms and molecules and leads from the initial to the final particles. Cross-section of the potential energy surface along the reaction path is called a profile reaction path. The difference between the potential energies of \(Q_0\) for the initial and final states is characterized by the energy change for the reaction. In particular, the heat of reaction \(Q\) is defined as the total change in potential energy \(Q_0\) and change the zero oscillation energy

\[
Q = Q_0 + \Delta E_z
\]

(1)

Here \(\Delta E_z\) is the difference of zero-point energies oscillation source and target molecules \(\Delta E = E_z - E'_z\). The presence of the potential barrier on the reaction path is typical for the most exchange chemical reactions (Fig. 1). The occurrence of this energy barrier is provided by the reconstruction of the electronic structure of molecules involved into the reaction that reduce the destruction of the chemical bond BC and the formation of a new bond AB [6]. This energy barrier is named the activation energy of a chemical reaction.

![Fig. 1. The way of the exchange reaction](image)

A + BC \(\rightarrow\) AB + C

Typically, the activation energy is < 1.5 eV for fast chemical processes, and slow processes are attributed with \(E_0 > 1.5\) eV.

Fig. 2 shows the profiles of the exchange process, taking into account the vibrational excitation of the molecule according to the Friedman Macharet model. The possibility to quantify the efficiency of the vibrational energy in chemical reactions was realized in this model [7].

As can be seen from the character of the chemical process profiles (see Fig. 2), the presence of the internal energy of the reagent leads to the reduction of the activation energy. The rate constant in the model is described by the expression

\[
k_R (E_\alpha) = k_0 \exp \left( \frac{-E_\alpha - \alpha E_z}{\theta} \right) \theta (E_\alpha - \theta E_z)
\]

(2)

The characteristic values of the coefficient \(\alpha\) are presented in Table and indicated a greater rate of the chemical reaction with internal states pumping in comparison with reaction without it.

![Fig. 2. Efficiency of vibrational energy in a simple exchange reaction A + BC \(\rightarrow\) AB + C. (a) Solid Curve – reaction profile; dashed line represents a vibronic term, corresponding to an atom A interaction with a vibrationally excited molecule BC\(^*\)(Ev); (b) part of the reaction profile near the summit of the exchange reaction barrier [7]](image)

<table>
<thead>
<tr>
<th>Coefficient of (\alpha)</th>
<th>0.9…1.00.2</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Endothermic</td>
<td>0.2…0.04</td>
<td>0.2</td>
</tr>
<tr>
<td>Exothermic</td>
<td>0.3…0.6</td>
<td>0.3</td>
</tr>
<tr>
<td>Termo-neutral</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

However, L.S. Polak [8] drew attention to the interesting relation of reaction rate constant \(k\) changes when vibrational states population temperature–\(T_v\) and translational temperature – \(T_t\) were changed. The experimentally studied reaction [9]:

\[
O^+ + N^* (v) \rightarrow NO^+ + N,
\]

(3)

was picked out for the illustration of this phenomenon.
The rate coefficient \( k \) increases 40 times when the \( T_v \) changes from 1000 to 6000 K (\( T_v = 300 \) K), but the same change in the translational temperature (no taking into account the \( T_v \) change) leads to significantly greater change in \( k \) – approximately 112 times according to Arrhenius expression \( k = A T_v^{\alpha} \exp (-E_a/RT) \) [10].

Using of the approach similar to the Fridman-Macheret \( \alpha \)-model for qualitative analysis of the influence of chemical processes on the increasing of the internal energy of the products (Fig. 3) indicates the growth of the activation energy of a chemical reaction for exothermic and endothermic processes. Although this growth is much smaller in the case of exothermic processes (see Fig. 3,a).

According to the Arrhenius law it indicates a lower reaction rate with the pump internal states of the reaction product compared to the reaction without pumping.

A large number of data on excitation of the products of elementary chemical processes vibrational levels was obtained in the study of atomic reactions. This research was initiated by Budartom and his colleagues [11]. The observed luminescence spectra of vibrationally excited hydroxyl reaction

\[
\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2 + 0.8 \text{ eV},
\]

(4) corresponding to transitions from the level \( v=9 \) and lower levels.

For the reaction

\[
\text{H} + \text{F}_2 \rightarrow \text{HF} + \text{F} + 1.06 \text{ eV}.
\]

(5) Jonathan, Melliar-Smith and Slater found that the share of the vibrational energy of HF molecules have to ~ 50% of the total energy released [6].

Theoretical analysis of the energy distribution in reaction products was first implemented by Evans and M. Polanyi in 1939–and based on Eyring and M. Polanyi conception of the chemical reaction \( \text{A} + \text{BC} \rightarrow \text{AB} + \text{C} \) as three particles \( \text{A}, \text{B} \) and \( \text{C} \) classical motion as a potential surfaces in one dimension (all three particles are on the same line). Evans and M. Polanyi revealed that in the case when the exothermic reaction energy is distinguished at the moment of atom \( \text{A} \) approaching to molecule \( \text{BC} \). Basic part of energy is converted into vibrational energy of the reaction product \( \text{AB} \). But if this energy is evolved in the process last phase, i.e. when \( \text{AB} \) and \( \text{C} \) are divorced, the molecule \( \text{AB} \) vibrational energy is small and the main part of the released energy takes the form of the reaction products translational energy. The case, which is realized in practice, is determined by the shape of the potential surface i.e. character of the dependence of the potential energy on the distance between the particles [6].

Also, the data on chemical lasers [12] analysis indicates that near half of released in the exothermic chemical reactions energy goes into increasing the translational temperature.

There is a growth of VT relaxation rate when temperature increases [5] and it leads also to a substantial increasing of the translational temperature during the exothermic chemical processes. There are additional factors, which increase the translational temperature of heavy component in chemically active plasma due to the chemical processes:

- the chemical processes in most cases are multi-stage [13];
- direct and inverse processes take place in statistical systems;
- the low-temperature plasma ability stimulates chemical processes that do not occur in standard chemical systems. Researches on plasma burning support (S. and A. Starikovskaya Starikovskii 2004, 2006) are shown that non-equilibrium plasma is able to stimulate the low-temperature oxidation of the fuel even without the combustible mixture ignition [14]. Kinetics investigations of the hydrocarbons partially-oxidative reforming supported by plasma are revealed simultaneous occurrence of hydrocarbons complete oxidation [15];
- a very high level of energy which is evolved during the exothermic chemical reactions (\( \geq 1 \) eV/molecule,
• e.g. \( \text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 = 2\text{CO}_2 + 3\text{H}_2\text{O} + 13.26\ \text{eV/molecule} \).

All mentioned above indicates that influence of chemical reactions on the level of plasma non-isothermality can be extremely high and directed to the reducing of the difference between the translational and internal states population temperatures due to the primary growth of heavy particles translational temperature at exothermic chemical reactions.

2. THE INFLUENCE OF CHEMICAL REACTIONS ON THE NON-ISOTHERMAL LEVEL OF PLASMA

Preliminary results of studies of the effect of exothermic chemical reactions on the level of nonequilibrium plasma transverse discharge (TD) and the discharge in the gas channel with liquid wall (DGCLW) were presented at [16].

The comparative analysis of plasma parameters of transverse arc and discharge in the gas channel with liquid wall was made for different working gas and liquids (air, distilled water and its mixtures with ethanol). Electron temperature \( T_e \) of atom excitations, molecule vibration \( T_v \), and rotation \( T_r \) temperatures in the generated plasma were determined by optical emission spectroscopy. Discharge realized in air or a lean mixture in the case of TD, and if DGCLW discharge were implemented in the air channel surrounded by the liquid distilled water and in the air channel surrounded by liquid ethyl alcohol (rich fuel mixture).

The methodological deficiency of [16] was the use of spectral bands of different molecules for the plasma without the fuel mixture and with the fuel mixture. So in the case of air plasma TD were bands of \( \text{N}_2 \), and plasma air / ethanol - CN band. The bands of \( \text{N}_2 \) and \( \text{OH} \) used for DGCLW burning in the air channel, surrounded by a liquid distilled water. And the bands of \( \text{C}_2 \) and CN molecules used for DGCLW burning in the air channel, surrounded by liquid ethanol.

In this paper we present the results of the evaluation temperature population of the vibrational levels - \( T_v \), and rotational levels- \( T_r \) plasma TD in the case of the discharge in the air flow and the flow of air mixtures with ethyl alcohol vapor from the emission spectra (Fig.4), which were recorded as the same and different molecular bands for plasma without fuel mixture (see Fig.4,a) and with the fuel mixture (see Fig.4,b).

As can be seen from Fig.4 the new results do not contradict the main conclusions of [16]:

• TD and DGCLW generate non-equilibrium plasma in the case of working gas air and working liquid – distilled water.
• Adding the fuel into the plasma system leads to the increasing of vibrational and rotational temperatures of molecules, which became equal to each other within the errors. This may indicate that the exothermic reactions reduce the level of non-thermality of the generated plasma as a result of additional energy supply for heavy components in the process of complete combustion of hydrocarbons.

3. ENERGY EFFICIENCY OF HYDROCARBONS REFORMING IN PLASMA AND PLASMA-CATALYSIS SYSTEMS

The plasma is a source of chemically active species (radicals, ions, excited atoms and molecules), and particles (electrons, photons) for chemical processes activating. This fact is enabled its use in a variety of technologies. Chemical technologies with plasma are usually constructed exclusively as plasma-chemical systems and hybrid systems. The plasma devices are fitted into standard chemical system at the last case. The first has the feature, when plasma is generated either in gaseous medium which is a mixture of starting reactants and some buffer gas (e.g., \( \text{Ar}, \text{N}_2 \)), or the starting reactants leading in the pre-ionized buffer gas stream. The various gas discharges, creating a non-equilibrium plasma, are used usually as plasma generators in the first case. The isothermal plasma acts as a heat-transfer medium in the second case. It has the \( 10^4 \) K temperature and products rapid quenching is required at the outlet of the reaction zone.

![Fig. 4. The emission spectrums of the transverse discharge plasma (gas: Air – a: Air+\( \text{C}_2\text{H}_5\text{OH} \) – b). Ratio of the concentrations of molecules \( \text{N}_2/\text{CN}/\text{N}_2/\text{NH}/\text{NO}/\text{O}_2/\text{OH} \) in the simulation:– \( 0.99/3.6\times10^7/1.6\times10^7/8 \times10^7/5\times10^7/5\times10^7/6\times10^7 \); b–0.77/1.2\times10^7/1\times10^7/4.5\times10^7/0.15/0.2\times10^7/2.7\times10^7]

In hybrid systems, a plasma generated reactive species stimulate a chemical process in the reaction chamber and is typically embedded in the proportion of plasma energy amounts to several percent of total process energy. This effect is called “plasma catalysis” [5]. Combined plasma-catalysis systems are constructed in a variety of configurations this is leaded to plasma
and catalysis synergy. One of such configurations is called plasma pre-treatment, when plasma is treated before entering in catalytic reactor. Another configuration, which is called plasma post-processing involves gas processing after exiting catalytic reactor.

It can be argued today that the problems of hydrocarbons plasma-chemical conversion into syngas (CO+H2) and other hydrogen-rich mixtures were solved using all known named above plasma-chemical systems and performed for a large number of hydrocarbons. Therefore, a comparative analysis, which is given for the various schemes effectiveness of just this chemical process, has the particular interest.

The partially-oxidative and steam reforming, their combinations are most completely investigated. There are following reactions in the case of ethyl alcohol reforming:

\[ \text{C}_2\text{H}_5\text{OH} + 1/2\text{O}_2 \rightarrow 3\text{H}_2 + 2\text{CO}, \]

\[ \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \rightarrow 4\text{H}_2 + 2\text{CO}. \]

Results of the different methods comparison are given in [17] for plasma ethanol reformer efficiency \( \eta \) by different methods of hydrocarbons conversion into syngas:

\[ \eta = \frac{\text{IPE} + \text{fuel injected} \times \text{LHV(fuel)}}{\text{fuel} \times \text{LHV(H}_2 \text{)} + \text{CO} \times \text{LHV(CO)}}. \]

Here LHV is defined as the lower heating values of each component. IPE is the input plasma energy.

This comparison indicates that selection of plasma reforming method has only a slight effect on \( \eta \). But comparison of these methods gives more significant differences between rates of electrical energy transformation into chemical (\( \alpha \)) by plasma-chemical method and the hybrid one.

\[ \alpha = \frac{\text{IPE} \times \text{LHV(H}_2 \text{)} + \text{CO} \times \text{LHV(CO)}}{\text{fuel} \times \text{LHV(fuel)}}. \]

It follows from the data given in Ref [5, 17, 18], that \( \alpha < 3 \) for ethanol reforming by plasma-chemical method and \( \alpha > 30 \) for hybrid plasma-catalysis one [5].

However, it should be noted that both components of the fuel mixture (air + fuel) are injected typically to plasma under partially-oxidation reforming by hybrid plasma-catalysis method. It should lead to a decrease in the level of non-equilibrium plasma conforming to the data presented in the previous sections. That is why the data which are obtained by Chernyakhovskij in researches on reforming of glycerol in the hybrid plasma-catalysis system with the low-power (50 W) gliding arc [19]:

- when both components of the fuel mixture are injected to plasma simultaneously, the maximum is \( \alpha \approx 60 \);  
- activating the plasma only oxidant \( \alpha > 250 \);  
- bigger efficiency exists in case, when only oxidizing agent is activated by plasma in ethanol reforming with hybrid plasma-catalysis method. It is shown at [20] where \( \alpha \approx 100 \).

CONCLUSIONS

1. The influence of chemical reactions on the level of non-isothermality of the plasma itself can be extremely high and aimed at the reducing of the discrepancy of the translational temperature from the temperature of energy level.
2. Our experimental researches demonstrate that even a small addition of ethanol into the non-equilibrium air plasma leads to the full disappearing of the difference between population temperatures of vibration and rotation states. The initial value of this difference is nearly several thousand degrees.
3. The full oxidation with plasma activation takes place under plasma formation in mixtures with very low fuel consistence.
4. The difference between \( T_v \) and \( T_n \) values increases due to the significant reduction of the translational temperature. It is occurred when inhibitor of the exothermic process is injected into the plasma-forming gas.
5. The transformation ratio of the electrical energy into the chemical energy is significantly higher at hydrocarbons reforming by the plasma-catalysis technologies than by the plasma-chemical technologies.
6. Transition from the plasma activation of both components of the fuel mixture to the plasma activation only oxidizer in the hybrid plasma-catalysis systems of the partially-oxidation reforming leads to the significantly increasing of the coefficient of the transformation of electric energy into the chemical energy of the produced syngas.

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REFERENCES

ПЛАЗМЕННЫЙ КАТАЛИЗ ХИМИЧЕСКИХ РЕАКЦИЙ

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Рассмотрены особенности реформирования этанола с учетом влияния экзотермических химических реакций на уровень неравновесности газоразрядной плазмы. Показано, что влияние экзотермических химических реакций на уровень неравновесности плазмы может быть чрезвычайно высоким и направленным на снижение отрыва поступательной температуры от колебательной температуры плазмы. Переход от активации плазмы обоих компонент топливной смеси к активации только окислителя в гибридных плазмокаталитических системах частично-окислительного реформинга приводит к существенному возрастанию коэффициента трансформации электрической энергии в химическую энергию полученного синтез-газа.

ПЛАЗМОВЫЙ КАТАЛИЗ ХИМИЧЕСКИХ РЕАКЦИЙ

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Розглянуту особливості реформування етанолу з урахуванням впливу екзотермічних хімічних реакцій на рівень нерівноважності газорозрядної плазми. Показано, що вплив екзотермічних хімічних реакцій на рівень нерівноважності плазми може бути надзвичайно високим і спрямованим на зниження відриву поступальної температури від коливальної температури плазми. Перехід від активації плазмою обох компонент топливної суміші до активації тільки окислювача в гібридних плазмокаталітичних системах частково-окисномого реформінгу призводить до істотного зростання коефіцієнта трансформації електричної енергії в хімічну енергію отриманого синтез-газу.