

PLASMA REFORMING OF ETHANOL IN DGCLW DISCHARGE

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This paper presents the results of experimental and theoretical investigations of the process of non-thermal plasma-assisted reforming of aqueous ethanol solutions in the dynamic plasma liquid systems using the DC electric discharges in a gas channel with liquid wall. The experiments show possibilities and efficiency of low-temperature plasma-chemical conversion of liquid ethanol into hydrogen-rich synthesis gas in different regimes. The numerical modelling clarifies the nature and explains the kinetic mechanisms of non-equilibrium plasma-chemical transformations in the plasma-liquid systems in different modes.

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1. INTRODUCTION

From physics and chemistry of fuel combustion it is known that addition of light inflammable gases (H_2 , CO) essentially improves ignition/combustion of heavy oil and bio-fuels [1]. Therefore hydrogen is considered as one of the most prospective energy sources for the future that can be renewable, ecologically clean and environmentally safe [2]. Among possible technologies for free hydrogen production, including steam reforming and partial oxidation of bio-fuels, a low-temperature plasma-assisted fuel reforming is believed to be a good alternative approach. Although the plasma reforming process needs some additional electric power, it has potential advantages: fast start-up, easy control, cooking reliability, compact design, etc provide good perspectives in its applications in aerospace technologies. For plasma fuel reforming, various methods using thermal and non-thermal plasma are known. Availability of use of low-temperature plasma is connected with possibility of reduction power inputs on overcoming level of the activations chemical reaction in condition of direct excitement oscillatory and rotational level of molecules. Such mechanism is more effective, than heating, for activation of chemical reaction [3]. One of the potential sources of non-thermal plasma that can provide simultaneously a high level of non-equilibrium and high density of reacting species in the plasma-liquid system is the electric discharge in a flowing gas channel with liquid wall (DGCLW). The main idea is that DGCLW can be burning directly within the liquid hydrocarbon fuels without preliminary gasification. Another peculiarity is that DGCLW can work in the bubbling microporous liquid which has a very large ratio of the plasma-liquid contact surface to the plasma volume.

The objective of this work is to develop and to study new methods of low-temperature plasma-enhanced reforming of liquid hydrocarbon fuels for applications in prospective plasma-assisted aerospace combustion technologies.

2. EXPERIMENTAL SET-UP

Experimental set-up for conversion of ethanol in synthesis – gas is shown on Fig. 1. It consists of a cylindrical quartz test-vessel (1) sealed at the top and at the bottom by duralumin flanges (2) with a built-in electrode system (3). The cooper rod electrodes (3) were inserted into the quartz tubes (4) and installed coaxially one opposite other. The tubes (4) served also for the gas (air) inlet. A compressed atmospheric air was injected along electrodes (3) through the open nozzle ends (4) and formed a stable counter-flow gas channel surrounding by liquid ethanol (6). The electric discharge (5) was burned in the gas channel between the immersed electrodes where an electric breakdown occurred. The ethanol/water solution (5 mole of ethanol : 1 mole of water) was filled into the reactor through the drain pipe (7) at the bottom flange. The outlet connections (8) and (9) at the top flange were connected with a system of communicating vessels allowing control of the liquid level and pressure in the reactor.

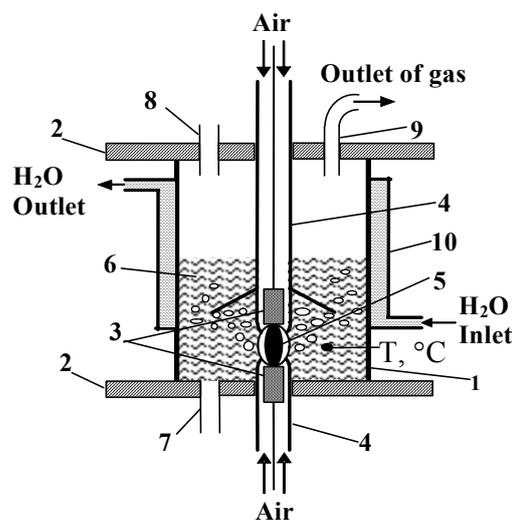


Fig. 1. Experimental set-up for conversion of ethanol in synthesis – gas

The outlet pipe (9) served for transportation of the synthesis gas products from the reactor to the condensing vessel and further to the gas analysis. Because of the electric-discharge heat release and heating of plasma-treated solution in the reactor, an auxiliary cooling was provided by the water-cooled jacket (10). The temperature of work solution in the reactor was measured by the immersed thermocouple.

The mass-spectrometric and gas chromatography techniques for investigation of stable gas-phase conversion products were used. The monopole mass-spectrometer was used for the mass analysis.

Various modes of the operation of the setup were studied: the mode where the voltage was applied to the electrodes mounted into the lower and upper flanges (the discharge was initiated between them); the mode where “+” was applied to the electrode mounted into the lower flange, whereas “-” was applied to the liquid (“liquid” cathode mode); the mode where “-” was applied to the electrode mounted into the lower flange, while “+” was applied to the liquid (“liquid” anode mode).

3. RESULTS AND DISCUSSIONS

The impact of the plasma-forming gas on the ethanol reforming in the DGCLW was studied. For that, the composition of gas-phase products of conversion in the reactor and the coefficient of energy transformation were studied at different gas flow rates. Research was conducted for the mode of solid electrodes. The composition and mixture ratio under the ethanol reforming was (5 mole of ethanol : 1 mole of water). The discharge current varied between 100 and 400 mA, the air flow rate varied from 0 to 110 cm³/s.

The results for discharge current $I = 100$ mA demonstrates a good matching between gas chromatography and mass-spectrometry data. For other currents the same matching is observed. It should be noted that with increasing air supply in the discharge the concentration of H₂ in syngas products decreases. In fact, the highest yield of H₂ is observed in the discharge mode without air supply. But the time of H₂ production in this case increases considerably, and the power consumption also increases. All this reduces the coefficient of energy transformation (Fig. 2). Moreover, this decreases the

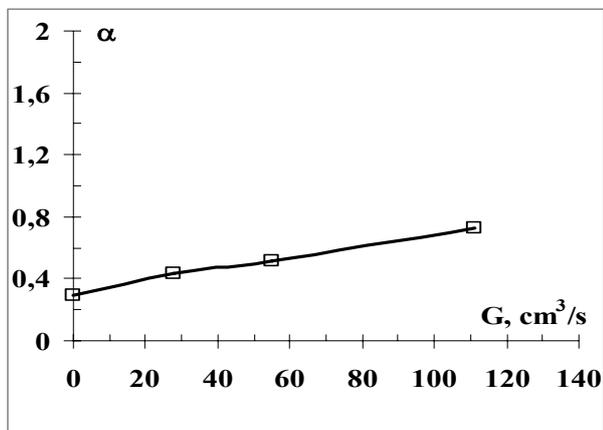


Fig. 2. Coefficient of energy transformation of the ethanol processing in the DGCLW as function of air flow rate. Ethanol-water solution (5/1), $I_d = 100$ mA, solid electrodes

lifetime of the system. Therefore, the total system performance without air supply seems to be not very good processing in the PLS with the DGCLW.

Fig. 3 shows the results of experiments and numerical modeling of concentrations of H₂, CO₂ and other main stable components in output gas products after the ethanol processing in the PLS with the DGCLW. The qualitative and quantitative agreement between calculated and measured data is quite good, at least, for main components. One can see that the output concentration [H₂] grows linearly with the discharge current and it reduces exponentially with the gas flow rate.

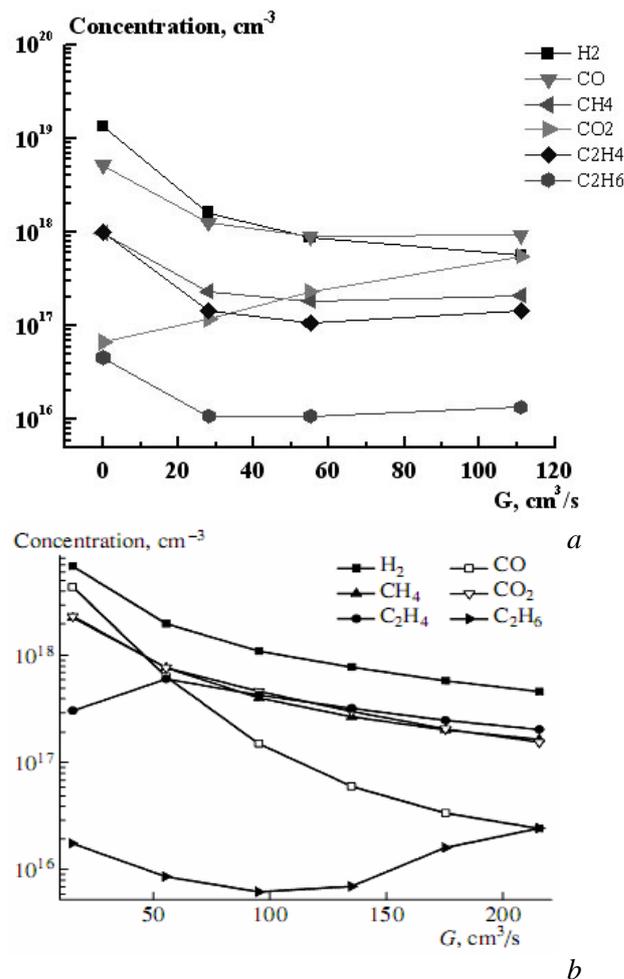
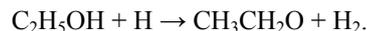


Fig. 3. The results of experiments (a) and numerical modeling (b) of concentrations of H₂, CO₂ and other main stable components in output gas products after the ethanol reforming, solid electrodes

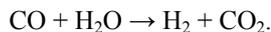
In the discharge conditions, the kinetics of the H₂ formation is determined mainly by the reaction



Since the ethanol concentration [C₂H₅OH] in solution changes slowly, the [H₂] production is determined entirely by the concentration of atomic hydrogen [H].

In the case under consideration, the main process responsible for the generation of H is the dissociation of water molecules H₂O by the direct electron impact. The rate of this process is proportional to the specific electric power deposited to discharge (i.e., discharge

current). Therefore, the $[H_2]$ production is also a linear function of the discharge current in accordance with experimental data. Outside the discharge, the only process that influences the H_2 concentration is the water-gas shift reaction



Via this process, the system reaches the complete conversion of CO into CO_2 and H_2 .

4. CONCLUSIONS

The dynamic plasma-liquid system with the electric discharge in a gas channel with liquid wall is quite efficient in plasma-chemical reforming of liquid ethanol into synthesis gas.

The composition content of syngas and the power inputs on the ethanol conversion in the DGCLW 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 a fairly good agreement with experimental data, at least, for the main syngas components, H_2 and CO , predicting a non-thermal plasma-chemical mechanism of the ethanol conversion in the investigated plasma-liquid system.

The numerical plasma-chemical kinetic modeling of the plasma conversion of ethanol into hydrogen in the DGCLW with the liquid electrode allowed understanding

the peculiarities and regularities of the processing in different regimes and conditions. It is found that the polarity of electrodes does not influence on the H_2 yield in the case when the work liquid is ethanol because the concentration of H_2 produced in the discharge in the mixture of air-ethanol vapors is many times larger than due to the electrolysis.

ACKNOWLEDGEMENTS

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REFERENCES

1. J. Warnatz, U. Maas, R.W. Dibble. *Combustion*. Berlin: "Springer", 2001.
2. *18th World Hydrogen Energy Conf.* 2010, Essen, Germany. <http://www.whec2010.com>
3. Z. Machala, M. Morvova, E. Marode, I. Morva. Removal of cyclohexanone in transition electric discharge at atmospheric pressure// *Journ. Phys. D: Appl. Phys.* 2000, v. 33, p. 3198-3213.

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ПЛАЗМЕННЫЙ РЕФОРМИНГ ЭТАНОЛА В РГКЖС РАЗРЯДЕ

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Представлены результаты экспериментальных и теоретических исследований процессов нетермического реформинга, поддерживаемого плазмой, водных растворов этанола в динамической плазменно-жидкостной системе с использованием электрического разряда постоянного тока в газовом канале с жидкой стенкой (РГКЖС). Эксперименты показывают возможность и эффективность низкотемпературной плазмохимической конверсии жидкого этанола в обогащенный водородом синтез-газ в разных режимах. Численное моделирование показывает природу и объясняет кинетические механизмы неравновесных плазмохимических преобразований в плазменно-жидкостной системе в разных режимах.

ПЛАЗМОВИЙ РЕФОРМІНГ ЕТАНОЛУ В РГКРС РОЗРЯДІ

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Представлено результати експериментальних та теоретичних досліджень процесів нетермічного реформінгу, що підтримується плазмою, водних розчинів етанолу в динамічній плазмово-рідинній системі з використанням електричного розряду постійного струму в газовому каналі з рідкою стінкою (РГКРС). Експерименти показують можливість та ефективність низькотемпературної плазмохімічної конверсії рідкого етанолу в збагачений воднем синтез-газ в різних режимах. Чисельне моделювання висвітлює природу та пояснює кінетичні механізми нерівноважних плазмохімічних перетворень в плазмово-рідинній системі в різних режимах.