PLASMA CONVERSION OF ETHANOL-WATER MIXTURE TO SYNTHESIS GAS

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We present the results of investigations of the ethanol conversion in a electric discharge in a gas channel with liquid wall (DGCLW). The parameters of the discharge in the liquid-wall gas channel are studied. The stable gas-phase products of the conversion are determined by using the mass-spectrometric technique and gas chromatography. The energy consumption in the conversion of ethanol to synthesis-gas is determined.

1. Introduction

Nowadays, one intensively searches for new liquid fuels that can substitute the traditional ones obtained from oil. That's why the investigations of the reformation of fuels aimed at the efficient control over the process of their combustion are very urgent. For example, it is known from physical and chemical aspects of combustion that the addition of light components to a fuel which have low temperatures of ignition and increase the speed of propagation of the combustion wave essentially improves the process of combustion. Among such components, we mention H_2, CO, and C_2H_2.

At the present time, the basic industrial methods of production of hydrogen are as follows: catalytic conversion of methane with water vapor; catalytic conversion of methane by a mixture of water vapor and oxygen; high-temperature non-catalytic conversion of methane in the presence of oxygen; water electrolysis in the presence of an acid or an alkali; and methane conversion in an arc discharge. From the ecological point of view, the processes of hydrogen production by means of the water electrolysis and in arc discharges are more attractive. However, due to a high level of consumption of the expensive electrical energy, they aren't widely used [1].

The present work considers the insufficiently investigated plasma method of reformation of ethanol on the basis of the electric DGCLW aimed at the production of synthesis-gas (te mixture of H_2, CO, and light C_xH_y). A characteristic specific feature of this method consists in the possibility of the external control over the composition of a plasma-forming gas.

2. Experimental Setup

The experimental setup used for the study of the conversion of hydrocarbon fuels is presented in Fig. 1. It includes quartz cylinder *1* which is hermetically sealed with duralumin flanges, into which a system of electrodes

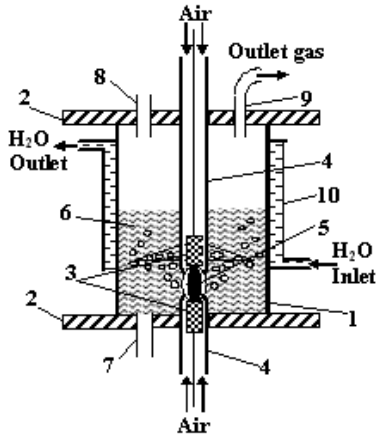

Fig. 1. Discharge in a liquid-wall gas channel

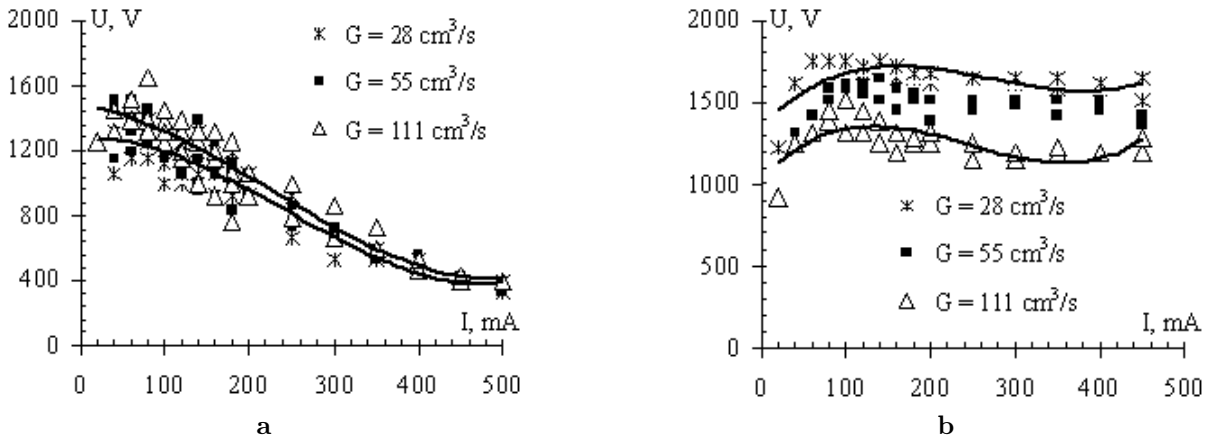

Fig. 2. Volt-ampere characteristics of the DGCLW: *a* – mode 1; *b* – mode 3

3 is mounted. The air supplied to glass tubes *4* with electrodes *3* flows around the electrodes from both sides and exits from the open ends of the tubes. Liquid *6* is poured into the reactor through tube *7*. The fluid level is maintained constant with the help of a system of connected vessels. The pressure in the reactor and in the system of connected vessels is maintained to be the same with the help of tube *8*. The upper flange has also a mounted tube *9* serving for the extraction of gases, which are formed during the plasma processing of the liquid, from the system. Air streams supplied through the lower and upper electrodes collide and form a stable gas channel between two electrodes. The electrodes are powered from a constant voltage source, which initiates discharge *5* burning in the liquid-wall gas channel. The lower and upper flanges are cooled with water, whereas the quartz cylinder has a water-cooling shell *10*.

The discharge channel in the liquid was formed in the following modes: with air delivery ($G \neq 0$) and without it ($G = 0$). As working liquids, we used ethanol, water, and ethanol-water mixture. Various modes of the operation of the setup were studied: *1* – the mode where the voltage was applied to the electrodes mounted into the lower and upper flanges (the discharge was initiated between them); *2* – the mode where "+" was applied to the electrode mounted into the lower flange, whereas "–" was applied to the liquid ("liquid" cathode mode); *3* – the mode where "–" was applied to the electrode mounted into the lower flange, while "+" was applied to the liquid ("liquid" anode mode).

We analyzed the composition of gas-phase products of the reformation for various operation modes of the setup by using various techniques: the mass spectrometric one and gas chromatography. For the mass spectrometric analysis of the gas, we used a monopole mass spectrometer MKh-7301 intended for the qualitative analysis of residual gases in vacuum systems with the pressure limits of operation equal to $10^{-4} \div 10^{-10}$ Torr. The pressure of residual gases in the analyzer didn't exceed 5×10^{-6} Torr. The pressure of used gases amounted to 5×10^{-5} Torr. The gas for the analysis was taken from the container using the piezoceramic valve.

When carrying out the gas chromatography analysis, a gas chromatograph 6890N produced by the Agilent firm was used. As a detector, we used a katharometer TCD (thermoconductometric detector) with a temperature of 200 °C, whereas argon served as a carrier gas.

3. Results and Their Discussion

The volt-ampere characteristics of the DGCLW are presented in Fig. 2. These characteristics are similar to those corresponding to the transient region from the anomalous glow discharge to the arc one. In the case of realization of mode *1*, the discharge passes from the anomalous glow to the arc one (Fig. 2,*a*). In the case of realization of mode *3*, the discharge doesn't pass to the arc mode (Fig. 2,*b*), which can be related to the fact that the carrying out of the material of the electrode to the discharge is practically absent. It can be caused by the good cooling of the electrode; in addition, a protective film can be formed on it. The behavior of the discharge in mode *2* is similar to that in mode *3*. Thus, choosing one mode or another, we can make plasma in such a system more nonequilibrium.

The amount of hydrogen H_2 in gas-phase products of the conversion strongly depends on the choice of a gas forming the channel. Figure 3 shows the mass spectra of gas-phase products of the conversion. In the case of a

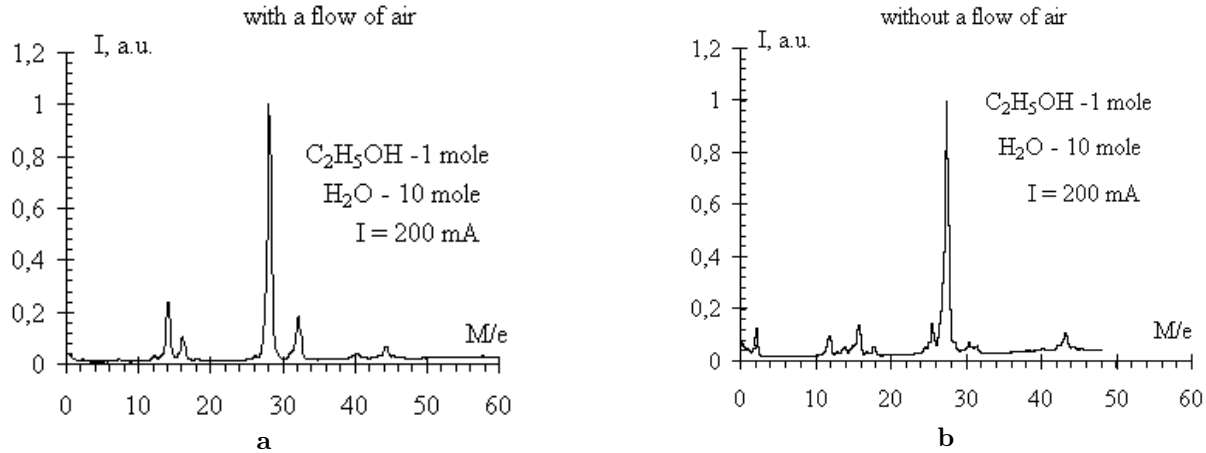

Fig. 3. Mass spectra the gas-phase products of the conversion: *a* – with air supply; *b* – without air supply

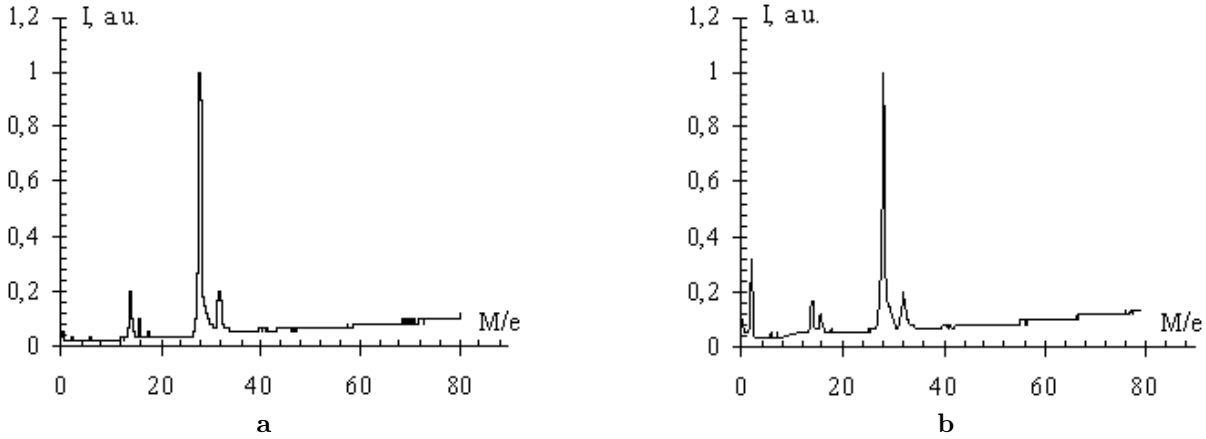

Fig. 4. Mass spectra of the gas-phase products of the conversion for mode *2* for discharge currents I_d: *a* – 30 mA; *b* – 250 mA. $G = 55$ cm^3/s

constant air supply to the discharge zone (Fig. 3,*a*), the mass spectra practically don't manifest the presence of hydrogen. But, in the case of realization of the mode of discharge burning without air supply (Fig. 3,*b*), one observes a rather large peak in the mass spectra corresponding to hydrogen. The mass-spectrometer measurements of the composition of the synthesis gas correlate well with the chromatographic measurements (Table 1).

Table 1

Gas-phase products of conversion	$G = 55$, cm^3/s	$G = 0$
H_2	5.92	40.38
O_2	14.48	12.48
N_2	64.64	18.0
CO	5.16	14.48
CH_4	1.37	5.7
CO_2	2.26	1.0
C_2H_4	0.99	2.3
C_2H_6	0.56	2.62
H_2O	1.85	0.68
C_2H_5OH	2.09	0.28
C_2H_2	0.68	2.08

Such a difference between the gas-phase products of the conversion can be related to the fact that, in the case of a constant air supply to the gas channel of the discharge, hydrogen generated in the process of conversion can be burning.

Figure 4 presents the mass spectra for mode *2* ("liquid" cathode). From these spectra, one can see that, in the case of the increase of the discharge current, the intensity of the peak corresponding to hydrogen rises.

The results of the gas chromatography investigations of the composition of gas-phase products of the conversion for mode *2* are given in Fig. 5,*a*. These results demonstrate that, in the case of the eightfold increase of the discharge current, the amount of H_2 rises by more

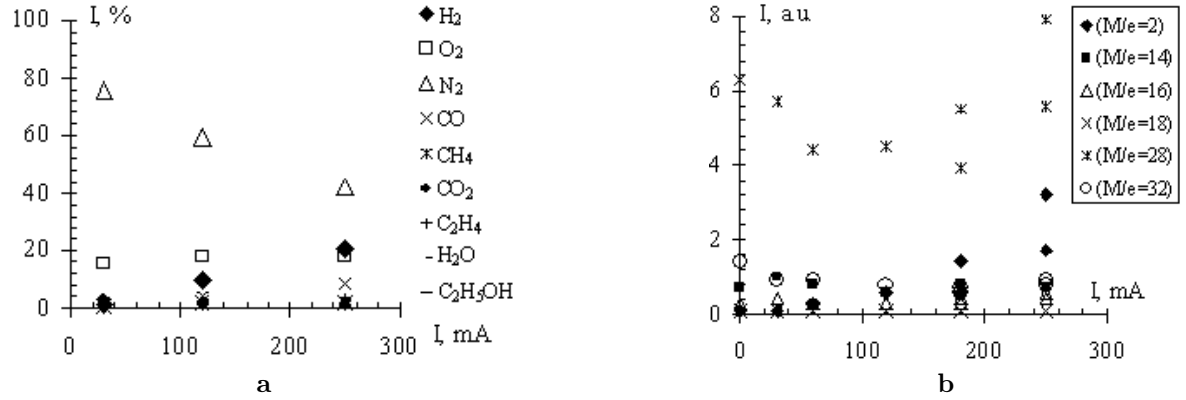

Fig. 5. Distribution of the composition of gas-phase products of the conversion depending on the discharge current (mode *2*): *a* – results of gas chromatography; *b* – results of the mass-spectrometric analysis

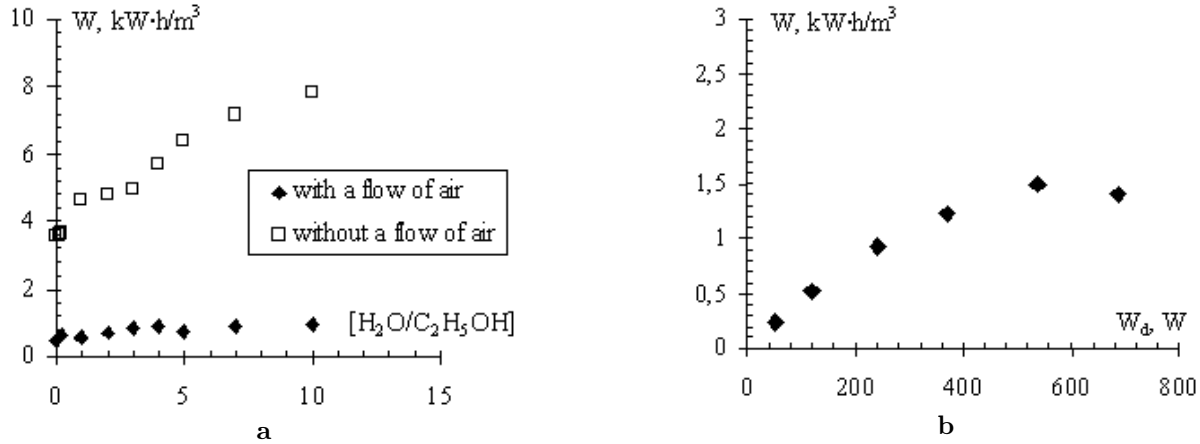

Fig. 6. Dependence of the energy consumption in the generation of gas-phase products of the conversion on the composition of the reformed mixture (*a*) and the discharge power (*b*). *a* – mode *1* ($I = 200$ mA; $G = 55$ cm^3/s); *b* – mode *2* ($G = 55$ cm^3/s)

than a factor of 20. Moreover, the amount of C_2H_4 increases approximately as much – by a factor of 17. The amount of CH_4 rises by a factor of 4.5 as well as CO by a factor of 5. At that, N_2 experiences a twofold decrease, whereas the amount of oxygen remains constant, which can testify to the fact that oxygen doesn't influence the process of reformation.

The results of gas chromatography studies correlate rather well with the mass-spectrometric measurements (Fig. 5,*b*). From the results presented in Fig. 5,*b*, one can see that the signal $M/e = 2$ corresponding to H_2 monotonically increases in the case of the rise of the discharge current, while the signal $M/e = 28$ corresponding to N_2 and CO nonmonotonically depends on the discharge current. Such a behavior of the signal can be related to the fact that, in the case of the increase of the discharge current, the amount of N_2 in gas-phase products of the conversion decreases, whereas the amount of CO essentially grows.

Figure 6 demonstrates the dependences of the energy consumption in the generation of gas-phase products of the conversion on the composition of the mixture treated in the reactor and the operation mode of the latter. As one can see from these dependences, the energy consumption in the generation of gas-phase products of the conversion in the electric discharge in the liquid-wall gas channel nonmonotonically depends on both the ethanol/water ratio in the mixture and the gas forming the channel in the liquid.

The minimal value of the energy consumption in the generation of synthesis-gas in the investigated modes amounted to 1.5 kW·h/m^3, which testifies to the prospects of the given method.

The work also deals with the estimation of the efficiency of the conversion of liquid hydrocarbon fuels in plasma of the discharge in a gas channel with liquid wall as compared to the other well-known plasma methods based on thermochemical calculations:

Table 2

	ITMO Belarus [1]	Korea [2]	Drexel USA [3]	MTI USA [4]	Shevcheko KNU Ukraine
Initial components	$CH_2 + H_2O$	$C_3H_8 + CO_2 + H_2O$	$CH_4 + 1/2(O_2 + 3.76N_2)$	Diesel	$C_2H_5OH + xH_2O + yO_2$
Power, kW	2	1.37	$0.5 - 10^*$	0.2	$0.05 - 1$
Energy value of synthesis gas, kW·h/m^3	–	2.28*	0.06	0.17*	1.45
Energy value H_2, kW·h/m^3	≤ 3	4.09*	–	2.19*	–
Productivity of H_2, m^3/g	0.48*	0.26*	–	0.091*	–
Productivity of synthesis gas, m^3/g	–	0.60*	–	1.2*	0.1
Total combustion heat of synthesis gas, kW·h/m^3	–	4.2*	2.9*	4.71*	7.71*
Energy efficiency	–	3	48	28	5.31

energy value of a cubic meter of synthesis-gas and hydrogen, productivity of each method, specific combustion value of the obtained synthesis gas, and energy efficiency of each method as the ratio of the combustion heat to the energy value. The calculations were performed with regard for the available thermal constants of the substances and the experimental data obtained by us and taken from the literature. The experimental data and results of the calculations (*) are given in Table 2.

4. Conclusions

The main stable gas-phase components at the output of the reactor in the case of the ethanol conversion are as follows: H_2, CH_4, C_2H_4, and CO whose amounts rise with an increase in the discharge current. The most intensively increasing component among them is H_2, whose concentration grows more than by a factor of 20 in the case of the eightfold increase of the discharge current.

The peculiarities of the behavior of the concentrations of O_2 (practically doesn't depend on the discharge current) and CO_2 (slightly falls with increase in the discharge current) on the parameters of the discharge can be related to an insignificant influence of the combustion on the reforming in the investigated modes.

The composition of gas-phase products of the conversion and the energy consumption in the conversion of ethanol to synthesis-gas in the electric discharge in the liquid-wall gas channel depend on the gas forming the gas channel.

The minimal value of the energy consumption in the investigated modes amounted to ~ 1.5 kW·h/m^3, whereas the energy stored in the conversion products is approximately equal to 5 kW·h/m^3, which testifies to the prospects of the given method.

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ПЛАЗМОВА КОНВЕРСІЯ СУМІШІ ЕТАНОЛ – ВОДА В СИНТЕЗ-ГАЗ

В.В. Юхименко, В.Я. Черняк, С.В. Ольшевський, І.В. Присяжневич, В.А. Зражевський, М.О. Веровчук, О.В. Соломенко, Я. Д. Скалній, С. Матейчік, В.П. Демчина, В.С. Кудрявцев, В.В. Наумов

Р е з ю м е

Представлено результати досліджень конверсії етанолу в електричному розряді з рідкою стінкою. Досліджено параметри розряду в газовому каналі з рідкою стінкою. Для визначення стабільних газофазних продуктів конверсії використовували масспектрометричну методику та газову хроматографію. Визначено енерговитрати на конверсію етанолу в синтез-газ.