

REFORMING OF BIOETHANOL IN THE SYSTEM WITH REVERSE VORTEX AIR/CO₂ FLOW OF “TORNADO” TYPE WITH LIQUID ELECTRODE

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In this paper we studied the reforming of bioethanol using the combined system that includes a plasma processing and handling in the pyrolysis chamber. As the plasma source was used plasma-liquid system with back-vortex flow of gas (a mixture of air and CO₂) and liquid electrode. Carbon dioxide was added in reforming the system to influence the plasma-chemical processes in the conversion of hydrocarbons. As the working fluid was used ethanol solution in distilled water (ratio C₂H₅OH/H₂O = 1/9,5). The system was investigated by emission spectroscopy, current-voltage characteristics, gas chromatography.

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INTRODUCTION

It is well known [1] that hydrogen (H₂) as the environmentally friendly fuel is considered to be one of the future most promising energy sources. Recently, interest in hydrogen energy has increased significantly, mainly due to the energy consumption increase in the world, and recent advances in the fuel cell technology. Because of the traditional fossil fuels depletion, today there's a growing interest in renewable energy sources (f.e. – bioethanol, biodiesel). Bioethanol can be produced from the renewable biomass, also it can be easily and safely transported due to its low toxicity, but it's not a very good fuel. It is common knowledge that [2] addition of the syngas to the fuel (H₂ and CO) improves the combustion efficiency: less burning time, rapid propagation of the combustion wave, burning stabilization, more complete mixture combustion and reduction of dangerous emissions (NO_x). As well, it should be taken into consideration that for efficient combustion (in terms of energy) of the synthesis gas it should contain more hydrogen, and in the case of the synthesis materials – they should contain more CO.

The main advantages of plasma-liquid systems are – high chemical plasma activity and good plasma-chemical conversions selectivity. Moreover, those are systems of atmospheric pressure and above, and this increases their technological advantages. Many modern energy projects have difficulties with the large amount of CO₂ storing and disposing. And it is also known that the addition of CO₂ to plasma during the hydrocarbons reforming may help to control plasma-chemical processes [3]. That is why the objective of the research is to study the influence of different amounts of CO₂ in the working gas on the plasma-chemical processes during the hydrocarbons conversion.

1. EXPERIMENTAL SETUP

The experimental setting is shown in Fig. 1. Its base is a cylindrical quartz chamber (1) with diameter of 90 mm and height of 50 mm. Top (2) and bottom (3) it is hermetically closed with metal flanges. Camera is filled with fluid (4), the level of which has been maintained by the injection pump through the hole (5). Bottom flange is made of stainless steel. The stainless steel T-shaped cylindrical electrode (6), cooled with water, immerses in the liquid through the central hole in the bottom flange. There is a 5 mm thick metal washer on its surface (7) in the middle of which there is a hole in diameter of 10 mm. Sharp corners are rounded. This washer is used for reducing the waves (which have been moving to the quartz wall) amplitude on the liquid surface.

The top flange, made from duralumin, contains copper sleeve (13) with a diameter of 20 mm is placed in the center (2), and plays the role of the second electrode. The nozzle with diameter of 4 mm and length of 6 mm is located in the center of the copper sleeve (8). Gas is introduced into the flange (2) through the aperture (9). Gas flow changes the direction at 90 degrees inside the flange and injects tangentially into the channel (10). The gas is rotated in the circular channel. Rotating gas (11) lands on the surface liquid and moves to the central axis of the system, where falls into the quartz cell (14) through the nozzle, forming a plasma torch (12). Camera (14), in its turn, plays a role of pyrolytic chamber. Flow rate reaches the maximum value near the nozzle. Due to this, the zone of lower pressure is formed in the center of the gas layer, compared to the periphery. The conical structure appears over the liquid's surface near the system axis (Fig. 1). External static pressure is 1 atm. and internal – 1,2 atm (during discharge burning). Gas from quartz

chamber (14) gets into the refrigerator (15), which is cooled with water at room temperature. Condensed matter (16) together with the gas from the refrigerator gets to the chamber (17). At the chamber exit (17) there's a flask (18), where gas is gathered for its composition diagnostics by means of mass spectrometry and gas chromatography. Study of plasma parameters is performed by emission spectrometry. The emission spectra registration procedure uses the system which consists of optical fiber (19), the spectral unit S-150-2-3648 USB (20), and the computer (21). Fiber is focusing on the sight line in the middle between the top flange (2) and the surface of the liquid (4). The spectrometer works in the wavelength range from 200 to 1100 nm. The computer is used in both control measurements process and data processing, received from the spectrometer. The voltage between the top flange and electrode, immersed in the liquid, is supplied by the power unit "PU". DC voltage provided is up to 7 kV. Two modes of operation have been considered: "liquid" cathode (LC) – electrode immersed in the liquid has "minus" and the top flange has "plus"; "solid" cathode (SC) - with the opposite polarity.

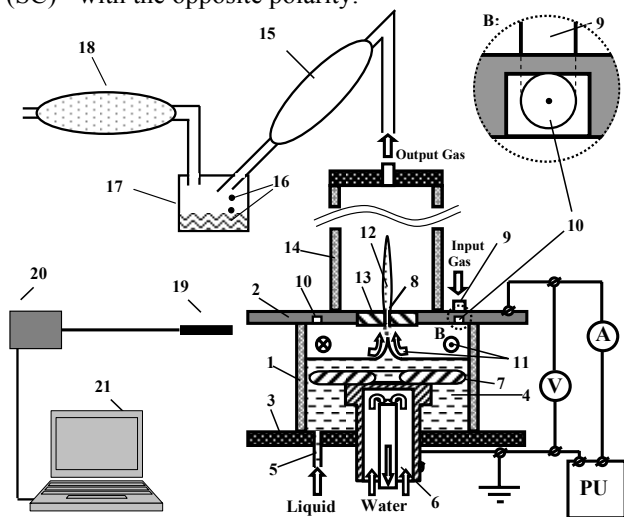


Fig. 1. Scheme of the TORNADO-LE plasma-liquid system with the vortex gas flow

For the analysis of the plasma-chemical processes kinetics the ethanol (ethyl alcohol solution in distilled water with a molar ratio $C_2H_5OH/H_2O = 1/9,5$), as a hydrocarbon model have been used. As the working gas mixture of air with CO_2 , in a wide range of air flow and CO_2 ratios has been used. The ratio between air and CO_2 in the working gas changes in the ranges: $CO_2/Air = 1/20 \div 1/3$ for the working fluid $C_2H_5OH/H_2O (1/9,5)$.

2. RESULTS AND DISCUSSIONS

The process of discharge ignition occurred as follows: the chamber is filled with liquid to a fixed level (5 mm above the washer). Liquid layer thickness of 5 mm has been chosen because that is the minimum liquid thickness in which the discharge burns between the liquid surface and the top flange. If the thickness is smaller plasma pushes the water toward the electrode immersed in the liquid and the discharge starts burning between two metal electrodes. Discharge goes into the arc regime. When the thickness of the distilled water layer above the washer is 5

mm (in the case of air flow only) break voltage reaches 4,5 kV and for a CO_2 flow - 6 kV. It is known [7], this increase in break-out voltage derives from the appearance of an additional loss channel of electrons – due to their sticking onto CO_2 molecules. This sticking has dissociative character and it is accompanied by the energy expense. For example, the threshold reaction with CO_2 is 3,85 eV. When the thickness of the $C_2H_5OH/H_2O (1/9,5)$ solution layer above the washer is 5 mm (in the case of air flow only) the break voltage is 5.5 kV, and for the air flow mixture with $CO_2 (CO_2/Air = 1/3)$ - 6, 5 kV. Adding CO_2 to the air leads to the increase in the break-out voltage value. Adding ethanol to distilled water ($C_2H_5OH/H_2O = 1/9,5$) results in the increase of break voltage on 1 kV. Power supply unit provides maximum voltage of 7 kV. Increasing the thickness of the fluid layer above the washer (> 5 mm) leads to the increase of the break-out voltage value. There is no discharge ignition with a break-out voltage value of more than 7 kV. Therefore, 5 mm thickness of the liquid layer above the surface immersed in a liquid metal electrode (washer) has been chosen as the optimum one.

The current-voltage characteristics show that adding a small amount of CO_2 (near 20%) of the working gas has no effect on the discharge type. In the range of flow ratios CO_2/Air from 1/20 to 1/5 characteristics are straight lines. It was observed that the increasing of CO_2 share in working gas causes discharge voltage supply rise.

The emission spectra show that when the working liquid is C_2H_5OH/H_2O solution (1/9,5), plasma contains the following components: atoms H, O, C, and hydroxyl OH. During the study, it turned out that the addition of CO_2 weakly affects the population temperature of excited electron, vibration and rotational levels of plasma components (Fig. 2) ($I = 300$ mA, $U = 1,9...2,4$ kV, air flow – 55 and 82,5 cm^3/s , the flow of CO_2 – 0; 4,25; 8,5; 17). Weak tendency to temperature decrease has been observed, but these changes do not exceed the error.

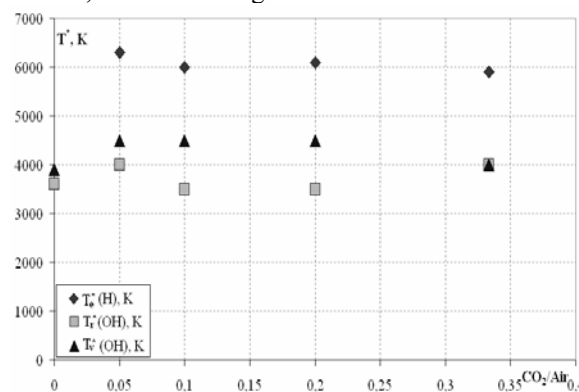


Fig. 2. Population temperatures of excited electron, vibration and rotational levels of plasma components at different ratio of CO_2/Air in the working gas

Fig. 3 shows the gas chromatography comparison of bioethanol conversion output products with and without the addition of CO_2 . The air flow is constant – 55 cm^3/s , in case of $CO_2/Air = 1/3$ – 17 cm^3/s of CO_2 has been added to the air (the total flow has been increased, which may explain the decrease in the percentage of nitrogen at a constant air flow; $I = 300$ mA, $U = 2...2,2$ kV). This histogram shows that adding of carbon dioxide leads to a

significant increase of the H₂ component percentage, CO (syngas) and CH₄ in the output gas. This may indicate that the addition of CO₂ during the ethanol reforming increases the conversion efficiency, because CO₂ plays a burning retarder role.

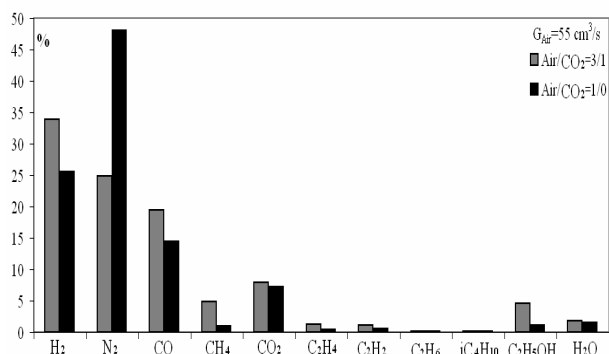


Fig. 3. Gas chromatography comparison of bioethanol conversion output products with and without the addition of CO₂

According to the gas chromatography, in the studied correlations range of CO₂/Air, syngas ratio ($[H_2]/[CO]$), changes slightly. Measurements were made by two air streams of 55 and 82.5 cm³/s and three CO₂ streams of – 4.25, 8.5 and 17 cm³/s; I = 300 mA, U = 2...2.2 kV.

Electrical energy transformation coefficient α has value of 0.81 for the "TORNADO-LE" type plasma-liquid system with an ethanol solution and pure air flow 55 cm³/s. And the CO₂ addition (the ratio of CO₂/air = 1/3) gives the value of $\alpha = 1,01$. System electrical parameters are as follows: I = 300 mA, U = 2...2.2 kV.

CONCLUSIONS

Carbon dioxide adding leads to a significant increase the percentage of H₂ + CO (syngas) and CH₄ components in the exhaust. This may indicate that the CO₂ addition under the ethanol reforming increases the conversion efficiency, because CO₂ plays a role of the retarder in the system by reducing the intensity of the conversion components combustion.

All the diagnostic methods, used in the "TORNADO-LE" PLS indicate that there're no NO_x compounds in the bioethanol and bioglycerol reforming products.

ACKNOWLEDGEMENTS

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РЕФОРМИРОВАНИЕ БИОЭТАНОЛА В СИСТЕМЕ С ОБРАТНОВИХРЕВЫМ ПОТОКОМ ВОЗДУХ/СО₂ ТИПА „ТОРНАДО” С ЖИДКИМ ЭЛЕКТРОДОМ

О.А. Недыбалюк, Е.В. Соломенко, В.Я. Черняк, Е.В. Мартыш, Т.Е. Лиситченко, Л.В. Симончик, В.И. Архипенко, А.А. Кириллов, А.И. Линтуга, Н.В. Беленок

Изучено реформирование биоэтанола с использованием комбинированной системы, которая включает плазменную обработку и обработку в пиролизической камере. В качестве источника плазмы была использована плазменно-жидкостная система с обратновихревым потоком газа (смесь воздуха и СО₂) и жидким электродом. Углекислый газ добавлялся в систему при реформировании для того, чтобы влиять на плазмохимические процессы конверсии углеводородов. В качестве рабочей жидкости использовался раствор этилового спирта в дистиллированной воде (соотношение C₂H₅ОН/Н₂О = 1/9, 5). Система была исследована с помощью эмиссионной спектроскопии, вольт-амперных характеристик, газовой хроматографии.

РЕФОРМУВАННЯ БІОЕТАНОЛУ В СИСТЕМІ ЗІ ЗВОРОТНОВИХРОВИМ ПОТОКОМ ПОВІТРЯ/СО₂ ТИПУ „ТОРНАДО” З РІДКИМ ЕЛЕКТРОДОМ

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Вивчено реформування біоетанола з використанням комбінованої системи, яка включає плазмову обробку і обробку в піролітичній камері. В якості джерела плазми було використано плазмово-рідинну систему зі зворотновихровим потоком газу (суміш повітря і СО₂) з рідким електродом. Вуглекислий газ додавався в систему під час реформування для того, щоб впливати на плазмохімічні процеси конверсії вуглеводнів. В якості робочої рідини використовувався розчин етилового спирту в дистильованій воді (співвідношення C₂H₅ОН/Н₂О = 1/9, 5). Система була досліджена за допомогою емісійної спектроскопії, вольт-амперних характеристик, газової хроматографії.