

PRODUCTS DETECTION AT ETHANOL CONVERSION IN ATMOSPHERIC PRESSURE GLOW DISCHARGE

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At the present one of the most important energy problems is to find alternative energy sources that would allow some to abandon the traditional hydrocarbon fuels such as gasoline, kerosene, methane, which is produced from oil and natural gas. Therefore, much attention is paid to the development of new methods of conversion of renewable hydrogen-containing compounds. Diagnostics of conversion products is carried out using the method of absorption infrared spectroscopy, gas chromatography and mass spectroscopy /1,2/. IR spectroscopy is a preferred method at a joint qualitative and quantitative analysis. However, it can not determine the concentration of non-polar molecules such as H_2 , N_2 and O_2 . Therefore, for the diagnostics of conversion products it is usually supplemented by chromatography or mass spectroscopy /1/.

This paper considers the diagnostics of ethanol conversion products in the plasma-chemical reactor the construction of which is based on three-electrode system used for the production of large volume glow discharges in various atomic and molecular gases /3,4/. For the conversion in the experiment, we used the mixture of ethanol (85%) with water (15%). If we have at the input of reactor the of alcohol-water mixture rate of 1.25 ml/min and air flow of 0.8 l/min, the reaction mixture composition can be estimated as follow: 57% of air, 30% of ethanol vapor and 13% of water vapor

The composition of conversion products of mixture after processing in a plasma reactor was determined by infrared absorption spectroscopy method. We used Fourier transform infrared spectrometer NEXUS (Thermo Nicolet). The absorption spectra were recorded in the range $400\text{--}4000\text{ cm}^{-1}$ with the resolution of 2 cm^{-1} . It was chosen a triangular apodization function, which leads to the line diffraction contours. For the spectroscopic analyze, exhaust gases from the plasma-chemical reactor were pumped through the 5- centimeter gas cuvette, which was previously heated up to $110\text{ }^{\circ}\text{C}$ in order to prevent condensation of water and alcohol vapors.

Intense vibrational-rotational bands of ethanol (900 , 1050 , 1250 , 1400 , 2950 and 3700 cm^{-1}), water vapor (1600 cm^{-1} , 3750 cm^{-1}), and much weaker bands of carbon dioxide molecules as component of the used ambient air in the laboratory are observed only in the IR absorption spectrum (Fig. 1, *a*) of initial

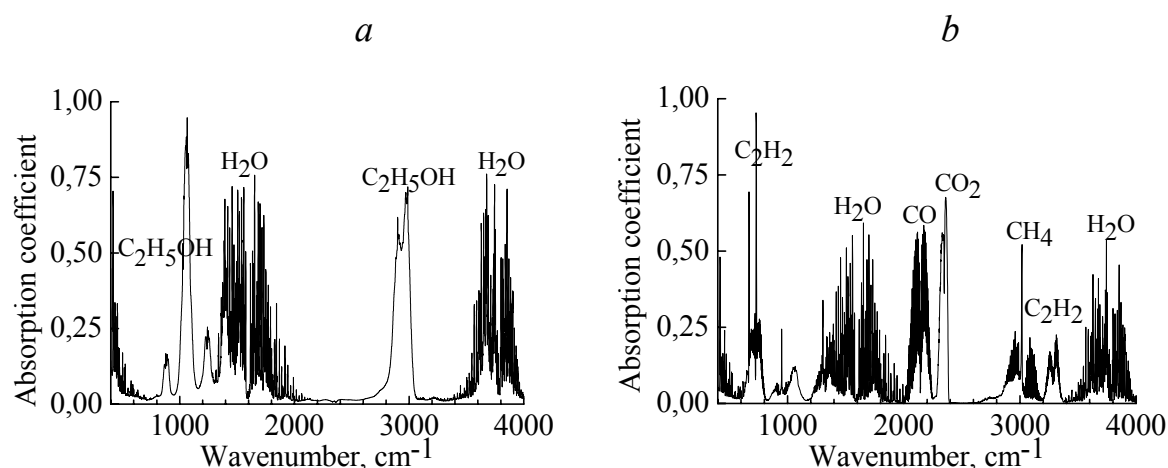


Fig. 1. Absorption IR-spectra of mixtures at the inlet (a) and outlet (b) of plasma reactor.

reaction mixture. The spectra were recorded by heating of the infrared spectrometer cuvette up to 110 °C.

After processing in a plasma the new bands belonging to the molecules of CH₄ (3100 cm⁻¹), CO (2200 cm⁻¹), C₂H₂ (750 and 3300 cm⁻¹) and CO₂ (740 and 2400 cm⁻¹) are observed (Fig. 1, b) in the spectrum of the mixture leaving the reactor. The weak intense absorption bands of ethanol and water are presented in spectrum as well.

Excluding the ethanol, mole fractions of all infrared active components in exhaust mixture were determined by comparison of the registered spectrum with calculated one. These spectra in the range of 2000 cm⁻¹–2400 cm⁻¹ are shown in Fig. 2. Calculation of absorption spectrum was fulfilled using the data base of Hitran [5]. The absorption in the range of 2000 cm⁻¹–2250 cm⁻¹ is

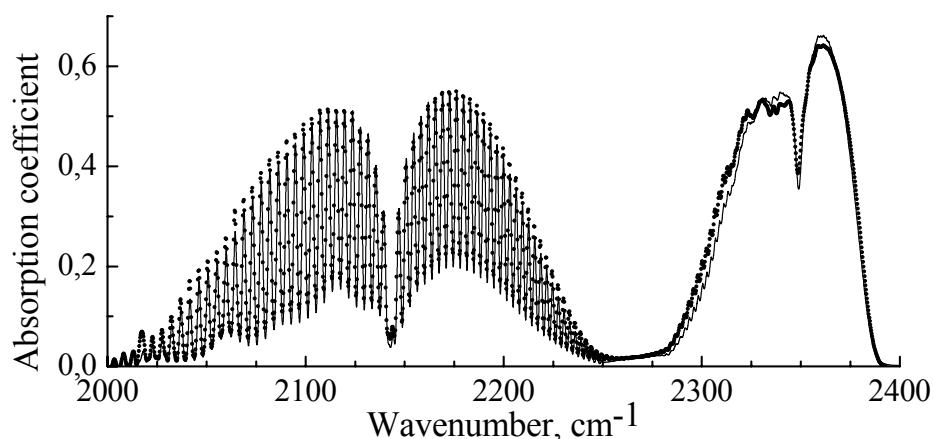


Fig. 2. Experimental (dotted) and calculated (solid) absorption IR-spectra of CO and CO₂.

determined by the CO molecules and we observed resolved the rotational line structure. In the range of 2250 cm^{-1} – 2250 cm^{-1} , absorption is defined by carbon dioxide molecules and due to smaller (compared to CO) distance between the rotation lines of CO₂ this band is unresolved. As you can see, there is good agreement between experimental and calculated data. The mole fractions of conversion products defined in this way are: $\{\text{C}_2\text{H}_5\text{OH}\}=0.3\%$, $\{\text{H}_2\text{O}\}=8\%$, $\{\text{CO}\}=23\%$, $\{\text{CO}_2\}=1.0\%$, $\{\text{CH}_4\}=1.2\%$ и $\{\text{C}_2\text{H}_2\}=0.8\%$. The mole fraction of ethanol was determined by experimental calibration curve of absorption, plotted using gas mixtures with known concentrations of alcohol.

The definition of hydrogen, nitrogen and oxygen mole fractions with the help of IR spectroscopy is not possible. Mole fractions of these components in exhaust mixture were calculated taking into account the composition of reaction mixture at the inlet of the reactor and the mole fractions of IR active components in the exhaust products determined experimentally.

So, we know the molar concentration of carbon components, that allow us to determine the number of carbonaceous molecules leaving a plasma reactor during one minute and distribute between them the number of carbon atoms containing in the input reaction mixture. Now, given the ratio of molar concentrations of water and carbon-containing component, it is easy to get the number of water molecules. Then, taking into account an equality of number of the hydrogen, oxygen and nitrogen atoms in the inlet and outlet mixtures one can easily calculate the number of relevant molecules leaving the plasma reactor per unit time, and determine the appropriate molar fraction, which are as follows: $\{\text{H}_2\}=36\%$, $\{\text{O}_2\}=0.1\%$, $\{\text{N}_2\}=21\%$.

The hydrogen concentration was also determined using the apparatus and the developed method for determining the concentration of H₂ in gas mixtures based on the inleakage of hydrogen through palladium membrane in previously evacuated volume [6]. Schematic diagram of setup is shown in Fig. 3, *a*. It consists of two volumes V1 and V2 divided by the palladium membrane PM. These volumes were previously evacuated by forepump. Palladium membrane was heated by the heater H. Then, the volume V1 was filled by gas mixture collected at reactor outlet. Hydrogen penetrates through membrane into volume V2. At the same time, the pressure growth rate dP/dt in this volume was registered by recorder RG. Fig. 3 *b* presents calibration curves for determination of hydrogen concentration in various mixtures of gases in the chamber V1 by maximum growth rate of the hydrogen pressure $(dP/dt)_{\text{max}}$ in the chamber V2. Curve 1 corresponds to H₂ and He mixture, curve 2 - mixture of H₂ and N₂, curve 3 - mixture of H₂, N₂ and CO with the ratio of the concentrations of $\{\text{CO}\}:\{\text{H}_2\}=1:1.5$. The ratio of mole fractions of CO and H₂ close to this value is characteristic for our experiments on ethanol conversion. The difference between the calibration curves is due to the difference of hydrogen diffusion

coefficient in the gas mixtures and different absorption degree of the gases at palladium surface. Using a calibration curve 3, we get $\{H_2\} = 35\%$, which is

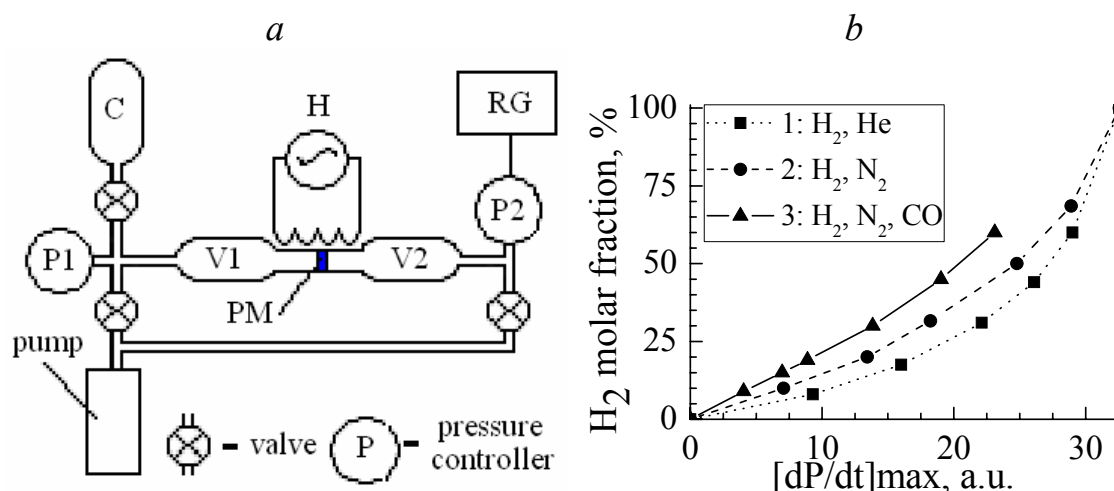


Fig. 3. Schematic of system of setup (a) and calibration curves for the determination of the molar fraction of hydrogen in the gas mixture (b).

close to the mole fraction of hydrogen, calculated using the data from the IR spectroscopy.

Thus, the infrared absorption spectroscopy together with the conservation equation for the number of atoms at the inlet and outlet of the reactor allows to determine the mole fraction of ethanol conversion products, including infrared inactive H₂, N₂ and O₂. The developed apparatus and method of determining the concentration of hydrogen in the gas mixture can control the concentration of H₂ in the process of ethanol conversion without making a detailed analysis of the composition of mixture.

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