

HYBRID PLASMA-CATALYTIC REFORMING OF ETHANOL INTO SYNTHESIS GAS: EXPERIMENT AND MODELING

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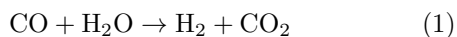
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Abstract. Understanding of the plasma-assisted reforming of hydrocarbons requires a combined application of the experimental studies of reforming systems and the kinetics modeling of reforming processes. Experiments were conducted on a system with a wide-aperture rotating gliding discharge with atmospheric air used as a plasma gas. Reforming parameters essential for the kinetics modelling of the reforming process were obtained. The influence of water addition method on the product composition of plasma-catalytic ethanol reforming was investigated.

Keywords: plasma-catalytic reforming, ethanol, synthesis gas, oxidative steam reforming.

1. Introduction

Synthesis gas produced during the reforming is commonly characterised by the volumetric concentration of H₂ and the ratio between H₂ and CO in the reforming products. Addition of water as a reforming reactant has shown to provide an additional source of H, O and OH species that initiate reforming reactions [1, 2] and can lead to better conversion efficiency and higher hydrogen content in the reforming products. In addition, the hydrogen content in the produced gas can be increased by converting CO using water via the water-gas shift reaction:



There are several ways of introducing water into the plasma-catalytic reforming systems, either directly into a discharge as a separate reactant or into a reaction chamber in a mixture with the hydrocarbon. The extent to which the method of water introduction impacts synthesis gas composition and H₂ yield during plasma-catalytic reforming remains under question. Understanding this topic requires a combination of experimental research and kinetics modelling of the processes inside the reforming system based on the operating parameters obtained during the experiments.

This work is focused on investigating the changes in the composition of the gas produced during the plasma-catalytic reforming of ethanol, which are caused by adding water as a reactant.

2. Experimental description

Plasma-catalytic reforming of ethanol was conducted via the partial oxidation reforming process (equa-

tion 2) and the oxidative steam reforming process (equation 3).

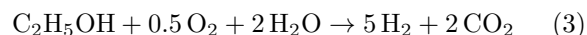
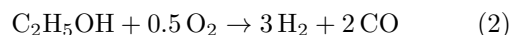


Figure 1 shows the scheme of the experimental setup used for the plasma-catalytic reforming of ethanol into synthesis gas. Reforming system used during experiments was created at the Taras Shevchenko National University of Kyiv. The system consisted of discharge chamber and reaction chamber, which were connected with each other. During the experiments, the food-grade ethanol was used for the conversion, atmospheric air was used as a source of oxygen and distilled water was used as a source of water.

All reactants were entering the system tangentially to the walls of discharge and reaction chambers, which led to the generation of vortex flows of reactants in both chambers. Air was supplied into the system using Fiac Cosmos air compressor. The total required airflow was separated and injected partly through the discharge chamber and partly through the reaction chamber. The airflow into each chamber was controlled using Dwyer RMA-22 SSV flowmeters. A flow of gas inside the discharge chamber caused a rotation of discharge channel. The part of air introduced into the discharge chamber was used to produce air plasma, which contained chemically active ions, free radicals and excited particles. Produced species were injected into the reaction chamber as a torch of rotating gliding discharge. The rest of the airflow was mixed with the ethanol or ethanol-water mixture, which was injected into the system at a specific rate using a syringe pump, and introduced into the reaction chamber.

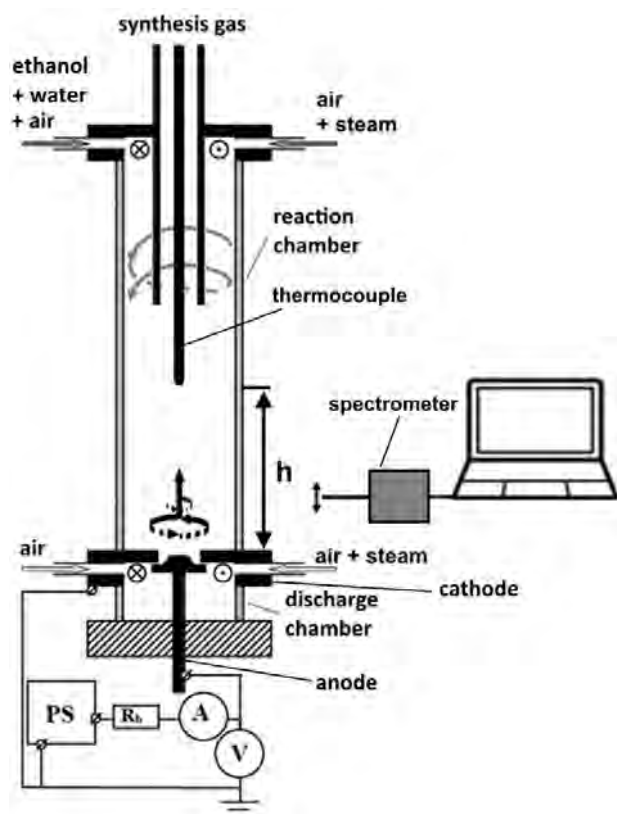


Figure 1. Scheme of experimental setup.

Plasma-catalytic reforming of ethanol was conducted in the cylindrical stainless steel or quartz reaction chamber 100 mm long and with 36 mm inner diameter. Type K thermocouple with 0.75 % T accuracy sleeve was introduced inside the ceramic into the reaction chamber via the outlet for the reforming products. This thermocouple measured the temperature inside the reaction chamber at the distance from the entrance into the reaction chamber from the discharge chamber (h) alongside the axis of the chamber.

Discharge system comprised central high-voltage stainless steel anode and grounded circular stainless steel cathode. Cathode had an aperture with 20 mm diameter. The distance between the electrodes was set to 1 mm. Rotating gliding discharge was powered using BP-100 power supply, which combined with the 33 k Ω ballast resistance R_b was able to apply up to 7 kV voltage to the discharge gap. During the reforming, the current of rotating gliding discharge was set to and maintained at specific value. The accuracy of current measurement was ± 5 mA and the accuracy of voltage measurement was ± 0.1 kV.

The introduction of the distilled water into the reforming system was done either as steam mixed with air and injected into the discharge or reaction chamber or as a liquid ethanol-water mixture introduced into reaction chamber. In case of the former, required steam flow was obtained by supplying 90 W of power to Kärcher SC1 steam generator.

Gaseous products obtained during the reforming

were cooled down to the room temperature using a water cooling system. This led to the condensation of excess water, leftover ethanol and heavy reforming products and their separation from the synthesis gas. Resulting gas was sampled and the volumetric concentrations of its components were determined via the gas chromatography on Agilent 6890 N gas chromatograph. Gas chromatograph used HP-MOLSIV and HP-PLOT Q columns thermostated in a temperature range from +4 to +450 °C, thermal conductivity detector at 200 °C and Ar carrier gas. Obtained volumetric concentrations were used to determine the specific gravity of produced synthesis gas in relation to air. The flow of produced gas was measured using Dwyer RMA-23 SSV flowmeter. This flowmeter was calibrated using air, therefore, calculated specific gravity of synthesis gas was used in the formula provided by the flowmeter manufacturer [3] to convert obtained flow measurements into the correct values of the synthesis gas flows.

Additional information about the optical emission spectroscopy of the radiation emitted out of the quartz reaction chamber in this system and rotational and vibrational temperatures of OH molecules inside the reaction chamber can be found in works [4, 5].

3. Results and Discussion

Temperatures inside the reaction chamber were measured for the 10 l min⁻¹ airflow into the discharge chamber and 5 l min⁻¹ airflow into the reaction chamber at distances h every 5 mm starting from 10 mm up to 65 mm. The range of the discharge current during the temperature measurements was from 20 mA up to 70 mA, with a 10 mA step. Average discharge voltage was 2.2 kV in the case of 20 mA and 1.6 kV for other currents. Figure 2 presents the obtained dependencies of the temperatures measured by the thermocouple at different distances h inside the reaction chamber on the discharge current.

Figure 2 shows that the temperature inside the reaction chamber increases with the rise of discharge current. This can be connected with the increased discharge power, which led to the higher specific energy input per mole of injected air. At the 20 mA discharge current, the temperature difference between the extreme positions of the thermocouples ($h = 10$ mm and $h = 65$ mm) is approximately 250 K, while at 70 mA this temperature difference increases to 500 K. Therefore, the temperature gradient between the hottest area of the reaction chamber, which is at the bottom of the chamber, and the reaction chamber exit increases with the rise of the discharge current and power. The gas temperature at the reaction chamber exit is approximately 1.5 times lower than near the bottom of the chamber. The temperature decrease can be caused by the mixing between the 10 l min⁻¹ airflow injected into the discharge chamber and heated by the discharge and the 5 l min⁻¹ airflow injected into the reaction chamber at room temperature.

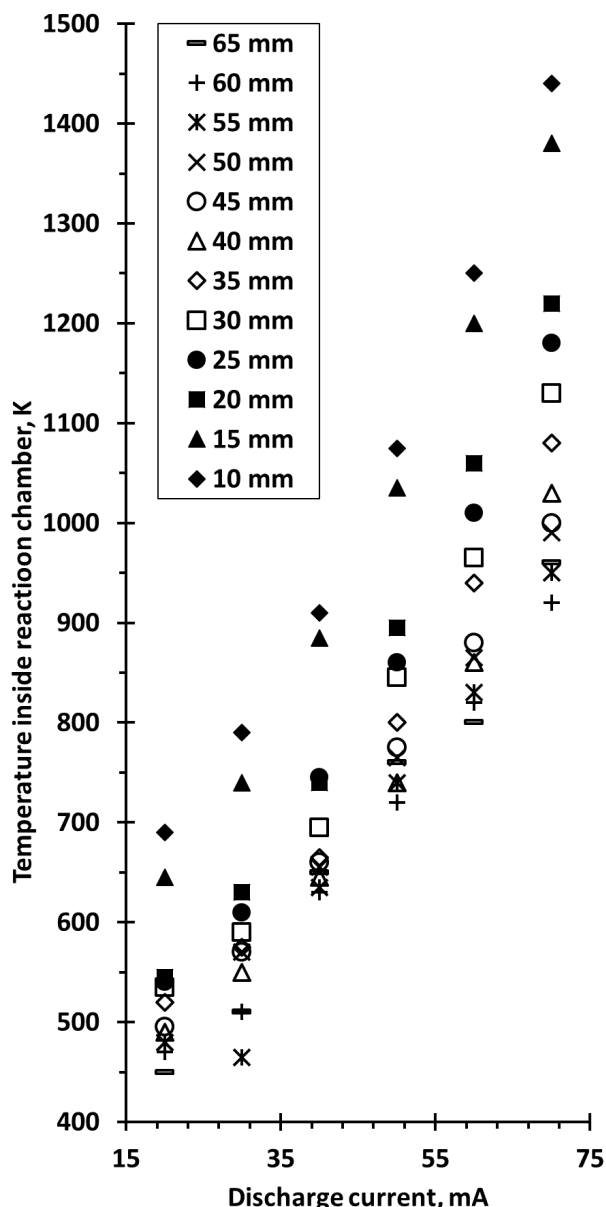


Figure 2. Temperatures at the specific distances h alongside the reaction chamber axis measured at the different discharge currents. Airflow into discharge chamber is 10 l min^{-1} , airflow into reaction chamber is 5 l min^{-1} .

The distributions of the gas temperature at the distance h along the reaction chamber axis measured by the thermocouple at 10 l min^{-1} airflow into the discharge chamber and 5 l min^{-1} and 7 l min^{-1} airflows into the reaction chamber are shown at figure 3. Temperatures were measured for 60 mA discharge current and 1.4 kV discharge voltage.

A slight rise of the temperature at the reaction chamber axis is becoming observable with the increase of the airflow into the reaction chamber. This increase is more noticeable closer to the discharge system at $h = 10 \text{ mm}$ than near the reaction chamber exit at $h = 65 \text{ mm}$. The rise of the airflow into the reaction chamber leads to the contraction of the discharge area inside the reaction chamber and to its restriction to

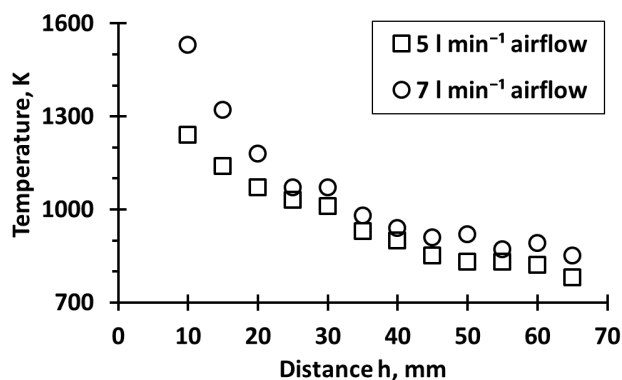


Figure 3. Distributions of temperature at distance h alongside the axis of the reaction chamber at 10 l min^{-1} airflow into discharge chamber, 5 l min^{-1} and 7 l min^{-1} airflows into the reaction chamber, discharge current is 60 mA and voltage is 1.4 kV .

Sample	Water addition method
1	Without water addition
2	2 g min^{-1} steam flow added into discharge chamber together with airflow
3	1 ml min^{-1} water flow added into reaction chamber together with ethanol as 1:11 water-ethanol mixture
4	2 ml min^{-1} water flow added into reaction chamber together with ethanol as 2:11 water-ethanol mixture

Table 1. Connections between the collected samples and water addition methods.

the chamber axis, away from the reaction chamber wall.

Several methods were used to introduce water into the reaction chamber during the investigation of the influence of water addition on the plasma-catalytic reforming of ethanol. Water was injected either as a steam-air mixture directly into the discharge or reaction chamber or introduced into the reaction chamber as liquid in ethanol-water mixture. In all cases the input ethanol flow was set to 648 ml h^{-1} . The airflow into the discharge chamber was kept at 10 l min^{-1} and the airflow into the reaction chamber was set to 5 l min^{-1} . Gas produced during the reforming was sampled for 4 different methods of water addition into the reaction chamber, which are presented in table 1. Figure 4 shows the volumetric concentrations of species in samples, which were obtained using gas chromatography.

The analysis of samples composition provided some insights into the impact of water addition method onto the reforming process. The addition of 2 g min^{-1} water steam flow into the discharge chamber (sample 2) led to the increase of the ratio between H_2 and CO in the produced gas from 0.95 (sample 1) to 1.4. In addition, the volumetric concentrations of H_2 and CO decreased, while several more complex hydrocarbons,

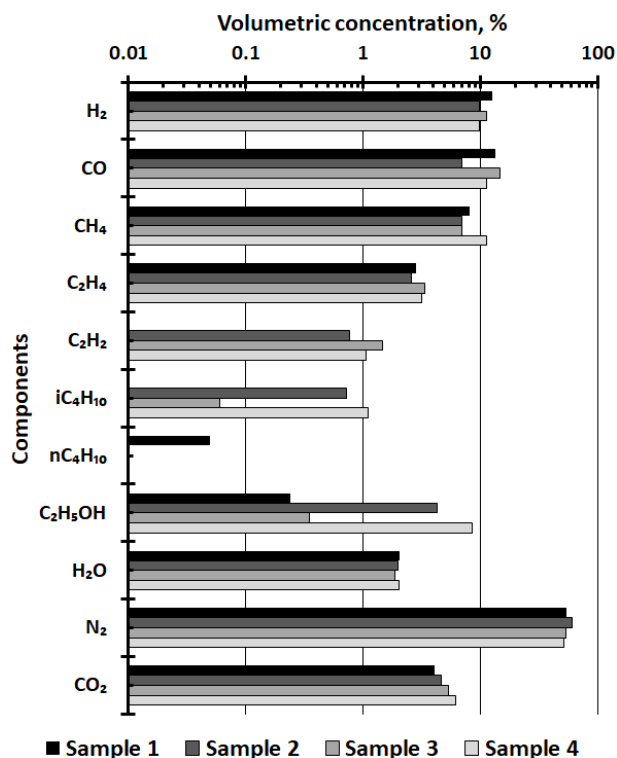


Figure 4. Volumetric concentration of species in gaseous reforming products obtained at 10 l min^{-1} air-flow into discharge chamber, 5 l min^{-1} air-flow into the reaction chamber, 648 ml h^{-1} ethanol flow into the reaction chamber, 60 mA discharge current and 1.4 kV voltage.

such as C_2H_2 and iC_4H_{10} , appeared in the products. In case of introducing water in a mixture with ethanol (samples 3 and 4), the ratio between H_2 and CO drops compared to the sample 1 to 0.77 for sample 3 but begins to recover with the increase of water percentage in a mixture and reaches 0.87 for sample 4. The volumetric concentrations of H_2 and CO decrease, C_2H_2 and iC_4H_{10} appear in the products, and the volumetric concentration of CH_4 increased in the case of water-ethanol mixture with the higher amount of water (sample 4). The introduction of water into both chambers led to the increase of CO_2 volumetric concentration in the reforming products. The rise of CO_2 concentration can be caused by the water-gas shift reaction (equation 1) or complete oxidation of hydrocarbons during reforming.

4. Conclusions

The highest measured gas temperature inside the reaction chamber is localized at the bottom of the reaction chamber near the exit from the discharge chamber. The temperature measured at the reaction chamber outlet is 1.5 times lower than the temperature near the discharge chamber. This temperature decrease may be caused by the addition of the air that was injected directly into the reaction chamber to the air that entered the reaction chamber from the discharge

chamber. The rise of discharge current and the consequent increase of the discharge power leads to the increase of the gas temperature along the reaction chamber axis. The rise of the airflow injected into the reaction chamber causes the increase of the gas temperature on the reaction chamber axis. This temperature increase can be caused by the airflow injected into the reaction chamber, which constricted the volume filled by the discharge and localized it closer to the reaction chamber axis.

The addition of water into the plasma-catalytic system during ethanol reforming leads to the increase of the volumetric concentrations of C_2H_2 , iC_4H_{10} and CO_2 . Addition of 2 g min^{-1} flow of water steam into the discharge chamber rises the ratio between H_2 and CO by 1.5 times in comparison to the reforming without water. The addition of 2 g min^{-1} flow of water in a mixture with injected ethanol provides the same ratio between H_2 and CO as the reforming of ethanol without water. This shows that activation of water in the discharge before its injection into the reaction chamber is preferable for the reforming process over the direct addition of water into the reaction chamber.

The impact of water activation on the reforming products can be connected to the increased production of H , O and OH species inside the discharge plasma, which are necessary for the initiation of the reforming reaction chains. However, a detailed modelling of the reaction kinetics is required for the understanding of this mechanism, which will be conducted in the future studies using the reforming parameters and plasma properties obtained in this study.

Acknowledgements

This work was supported by the state grant of the Ministry of Education and Science of Ukraine 0118U002057.

References

- [1] A. I. Shchedrin, D. S. Levko, V. Y. Chernyak, V. V. Yukhimenko, and V. V. Naumov. Effect of air on the concentration of molecular hydrogen in the conversion of ethanol by a nonequilibrium gas-discharge plasma. *JETP Letters*, 88(2):99–102, 2008. doi:10.1134/S0021364008140063.
- [2] A. Frassoldati, A. Cuoci, T. Faravelli, and E. Ranzi. Kinetic Modeling of the Oxidation of Ethanol and Gasoline Surrogate Mixtures. *Combustion Science and Technology*, 182(4-6):653–667, 2010. doi:10.1080/00102200903466368.
- [3] Dwyer Instruments. Variable Area Flow Corrections. [2018-11-16]. URL: <http://blog.dwyer-inst.com/2017/09/06/variable-area-flow-corrections/#sthash.syxIW2q1.dpbs>.
- [4] I. I. Fedirchuk, O. A. Nedybaliuk, V. Y. Chernyak, and V. P. Demchina. Plasma-catalytic reforming of rich ethanol-air mixtures. *Problems of Atomic Science and Technology*, (1):164–167, 2019.
- [5] O. A. Nedybaliuk, I. I. Fedirchuk, and V. Y. Chernyak. Plasma-catalytic system with wide-aperture rotating gliding discharge. *Problems of Atomic Science and Technology*, (6):214–217, 2018.