

REFORMING OF ETHANOL IN HYBRID PLASMA CATALYTIC SYSTEM

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Influence of reaction chamber material on the hybrid plasma-catalytic reforming of model hydrocarbon was studied using same size quartz and steel reaction chambers. NO bands were shown to disappear from the plasma emission spectra during the ethanol reforming. Reforming in steel reaction chamber showed higher reforming efficiency and hydrogen energy yield than the reforming in a quartz reaction chamber.

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INTRODUCTION

Hybrid plasma-catalytic approach allows to conduct chemical transformation of complex raw materials at the non-equilibrium conditions and low temperature, which makes it attractive for creating technologies compliant with the green chemistry requirements. In the case of hydrocarbon raw materials, this approach is the foundation for the hybrid plasma-catalytic reforming. The study of hybrid plasma-catalytic reforming showed that it is an effective method of producing synthesis gas from hydrocarbons. However, most aspects of this process and ways it is influenced by the external factors remain uninvestigated. The influence of the reaction chamber material on the reforming process and its products is one of such unanswered questions.

1. EXPERIMENTAL SETUP AND METHODS

Steel chamber had quartz windows, which allowed to observe the processes inside the chamber during the reforming. Thermocouples were used to measure the temperatures at both ends of the reaction chamber.

Fig. 1 shows the scheme of the plasma catalytic system with rotating gliding discharge used for the conversion of liquid hydrocarbons into synthesis gas. Reforming system (see Fig. 1) has two connected chambers: discharge chamber and reaction chamber. Ethanol was used as a model hydrocarbon. Oxygen was used as a model oxidant. The flow of air that was needed for the reforming was divided between discharge chamber and reaction chamber. Part of the air that is introduced into the discharge chamber is activated by a discharge and becomes a source of active species. After the activation in the discharge chamber, the air is introduced into the reaction chamber as a torch. The mixture of the ethanol with the rest of the air is introduced through the top of the reaction chamber. In both chambers, air flow is introduced tangentially to the wall and rotates clockwise relative to the top-down perspective from the synthesis gas output. The discharge and reaction chamber air flows form a vortex and a tornado-type reverse vortex flows, respectively. The study of the plasma-catalytic reforming of ethanol was conducted using quartz and metal reaction chambers with 100 mm height and 36 mm internal diameter. The discharge was ignited between the internal T-shaped stainless-steel anode electrode with 25 mm diameter and the external ground-

ed stainless-steel ring cathode, which contains aperture 20 mm in diameter.

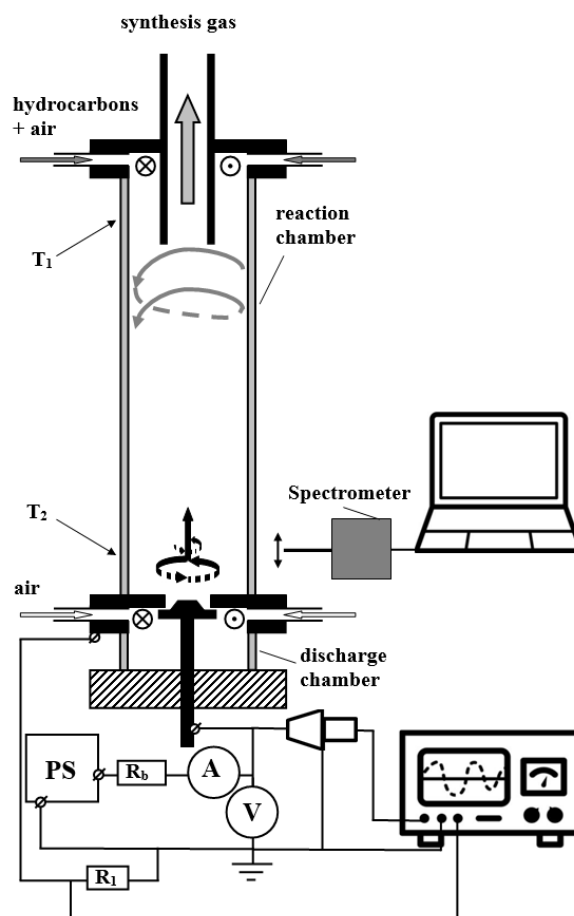


Fig. 1. Scheme of the hybrid plasma-catalytic system with rotating gliding discharge for the reforming of liquid hydrocarbons into synthesis gas

Power was supplied to the rotating gliding discharge via the БП-100 power source (PS), which provided 7 kV voltage at 33 k Ω ballast resistance (R_b). Discharge voltage and current were measured using a voltmeter and an ammeter. Voltage and current oscillograms were obtained using a digital oscilloscope, 1/480 voltage divider and 10 Ω measuring resistance (R_1).

Optical emission spectra of the plasma torch radiation in the quartz reaction chamber were registered using a system consisting of an optical fiber, Solar TII (S-150-2-3648 USB) spectral device and a PC. Spectrome-

ter operated in a wavelength range from 200 to 1000 nm. PC was used for controlling measurements and processing data obtained from the spectrometer.

Required temperature of the reaction chamber was maintained via the increase of the input air flow, which led to the complete oxidation of the part of ethanol inside the reaction chamber. Reaction chamber temperature was measured using two thermocouples, which were connected to the top (T_1) and bottom (T_2) of the reaction chamber at 10 mm distance from the top and bottom flanges, respectively.

The air flow introduced inside the discharge chamber was equal $10 \cdot \text{l} \cdot \text{min}^{-1}$ and the air flow inside the reaction chamber was $5 \cdot \text{l} \cdot \text{min}^{-1}$. Based on the bottom thermocouple measurements, the temperature of both reaction chambers during the gas sampling was 200°C . The composition of the gaseous reforming products was determined using Agilent 6890 N gas chromatograph. The total flow of produced gas was determined using Dwyer RMA-22-SSV and RMA-23-SSV rotameters. The photographs of the system during its operation were done using Nikon™ D7100 camera. Total input air flow ($15 \cdot \text{l} \cdot \text{min}^{-1}$) was larger than required for the partial oxidation reaction (1) stoichiometry. The flow of 96% ethanol was $486 \text{ ml} \cdot \text{h}^{-1}$ (3 kW), which corresponds with reaction (2) stoichiometry:

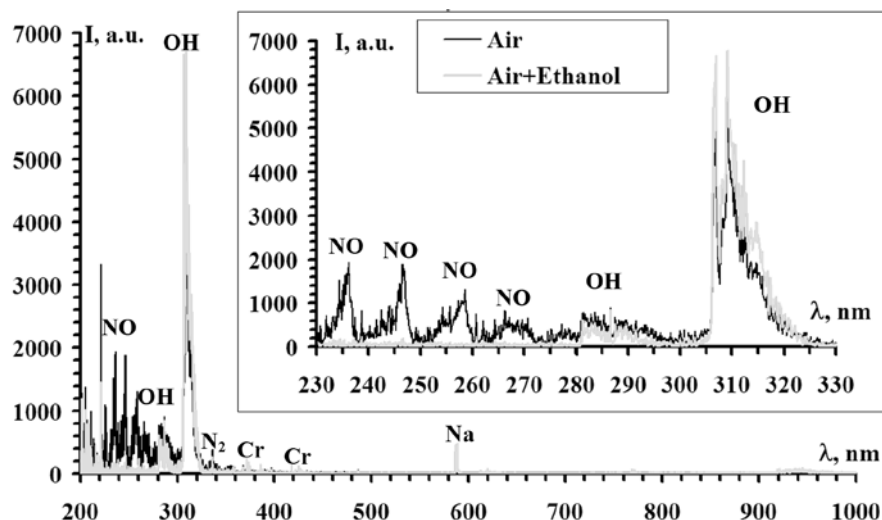
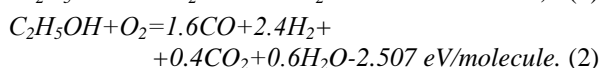
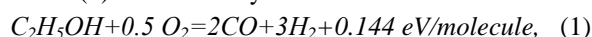


Fig. 3. Optical emission spectra of the rotating gliding discharge plasma torch radiation without ethanol input and during the hybrid plasma-catalytic reforming of ethanol

In case of air without ethanol, the emission spectra (Fig. 3) contain only bands of hydroxyl OH, nitrogen monoxide NO and low-intensity band of nitrogen N_2 . The introduction of 96% ethanol ($486 \text{ ml} \cdot \text{h}^{-1}$) led to a disappearance of NO band from the emission spectra and a slight decrease of the N_2 band intensity, however, it caused the appearance of chrome (Cr) and sodium (Na) multiplets in spectra (see Fig. 3). NO bands could disappear in response to the start of H_2 production after the introduction of ethanol, which reduces NO by removing oxygen. Chrome is a part of electrode material and sodium Na can be present in a quartz that composes reaction chamber as well as in ethanol because it is food-grade. NO bands reappeared, and Cr and Na dis-

2. RESULTS AND THEIR DISCUSSION

Fig. 2 shows the typical voltage and current oscillograms of the rotating gliding discharge.

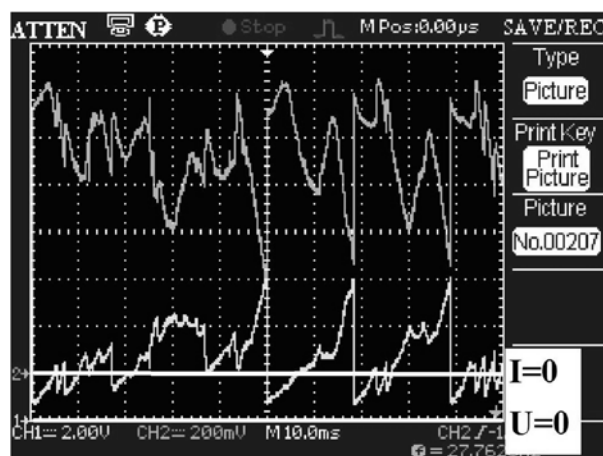


Fig. 2. Typical oscillograms of rotating gliding discharge voltage (CH1, yellow) and current (CH2, blue) at $10 \text{ l} \cdot \text{min}^{-1}$ flow inside the discharge chamber, voltage divider coefficient is $1/480$, resistance for measuring current is 10Ω

Fig. 3 shows optical emission spectra of the rotating gliding discharge plasma torch inside a quartz reaction chamber with air as a working gas without ethanol and during the hybrid plasma-catalytic reforming of 3 kW ethanol flow ($486 \text{ ml} \cdot \text{h}^{-1}$).

appeared from the spectra after the termination of ethanol input.

The change of the input ethanol flow did not lead to the change of rotational and vibrational temperatures of species inside the torch.

Ethanol introduction leads to the torch increase in systems with both quartz and metal reactor chambers, however, in case of a quartz chamber torch was longer than in case of a metal chamber. In addition, the color of synthesis gas flame at the system exit was different and had a yellow hue in case of quartz chamber. The increase of torch length can be caused by the presence of the exothermic reactions of complete ethanol oxidation.

Fig. 4 shows the volumetric concentration of the main synthesis gas components during the hybrid plasma-catalytic reforming of ethanol using quartz and metal reaction chambers and 486 ml·h⁻¹ (3 kW) ethanol flow. The air flow into the discharge chamber was 10 ·l·min⁻¹ and air flow into the reaction chamber was 5 ·l·min⁻¹. The temperature of the reaction chamber dur-

ing the gas sampling was 200°C based on the bottom thermocouple readings.

The change from quartz to metal reaction chamber was accompanied by the increase of hydrogen H₂ and carbon monoxide CO amount, meanwhile, the quantity of other main components remained practically unchanged (see Fig. 4).

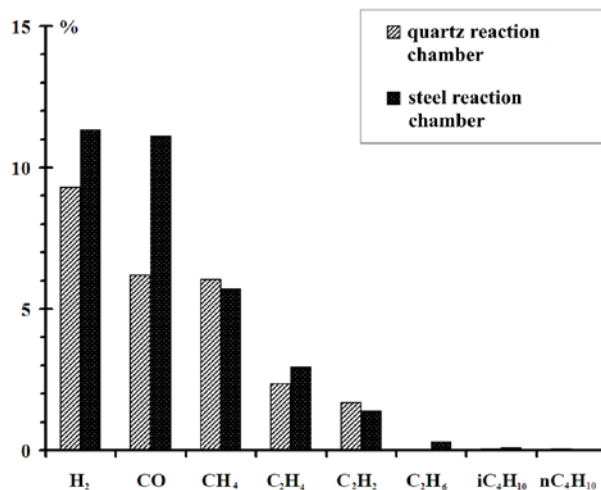


Fig. 4. Volumetric concentration of main synthesis gas components during hybrid plasma-catalytic reforming of ethanol using quartz and metal reaction chambers, ethanol flow is 486 ml·h⁻¹ (3 kW), air flow into discharge chamber is 10 ·l·min⁻¹, air flow into discharge chamber is 5 ·l·min⁻¹, reaction chamber temperature based on bottom thermocouple readings is 200°C

Fig. 5 shows the volumetric concentration of non-combustible components and unreacted ethanol in synthesis gas during the hybrid plasma-catalytic ethanol reforming. The amount of nitrogen N₂ slightly decreased, which indicates the increase of synthesis gas

flow. The amount of CO₂ decreased as well, which can explain the increase in CO amount. Oxygen O₂ is absent in both cases, which indicates that it was completely used in reactions.

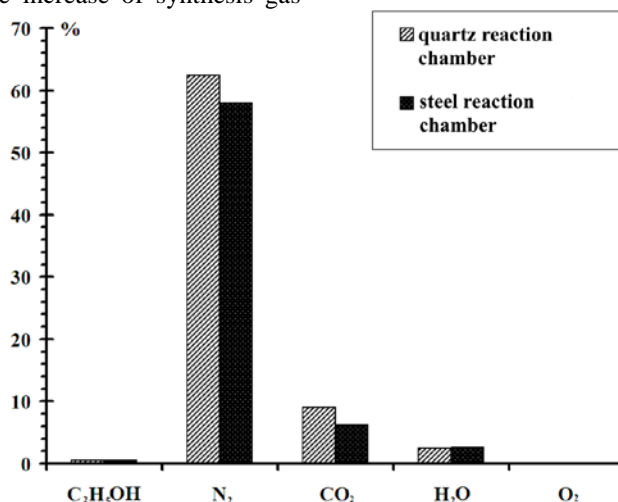


Fig. 5. Volumetric concentration of non-combustible components and unreacted ethanol in synthesis gas during hybrid plasma-catalytic reforming of ethanol using quartz and metal reaction chambers, ethanol flow is 486 ml·h⁻¹ (3 kW), air flow into discharge chamber is 10·l·min⁻¹, air flow into reaction chamber is 5 l·min⁻¹, reaction chamber temperature based on bottom thermocouple readings is 200°C

Obtained data on product composition enables the calculation of reforming efficiency (η) using equation [1]: $\eta = (LHV_{products} G_{products}) / (P_{plasma} + LHV_{reactants} G_{reactants})$, (3) where $LHV_{products}$ – total lower heating value of all gaseous reforming products not including the unreacted reactants; $G_{products}$ – total flow of gaseous reforming products; P_{plasma} – energy spent on plasma generation in a unit of time; $LHV_{reactants}$ – total lower heating value of all reactants; $G_{reactants}$ – total flow of all reactants.

Ratio between the chemical energy of reforming products and electrical energy spent on plasma generation is determined using equation:

$$\alpha = (LHV_{products} G_{products}) / P_{plasma} \quad (4)$$

This value indicates in how many times the thermal energy obtained from the combustion of produced synthesis gas is higher than the energy required for the plasma generation (oxidant activation).

Hydrogen production efficiency in the system can be evaluated using its hydrogen energy yield $E_Y(H_2)$ [g/kWh]. It corresponds to the flow of produced hydrogen $G(H_2)$ [g/h] divided by the power spent on plasma generation P_{power} [kW]:

$$E_Y(H_2) = G(H_2)/P_{plasma} \quad (5)$$

Table shows parameters of hybrid plasma-catalytic reforming of ethanol in quartz and metal reaction chamber.

Reaction chamber type	quartz	metal
Power (kW)	3	3
Ethanol flow (ml·h ⁻¹)	486	486
Air flow (l·min ⁻¹)	15	15
Synthesis gas flow (l·min ⁻¹)	17.5	18
Ratio α (kW/kW)	14	17
Reforming efficiency (η , %)	57.3	68.9
Hydrogen energy yield ($E_Y(H_2)$, g/kWh)	72.5	90.9
Syngas ratio H ₂ /CO	1.5	1

Parameters of hybrid plasma-catalytic reforming of ethanol in quartz and metal reaction chamber

A transition from quartz to metal reaction chamber causes 1.5 times decrease of syngas ratio H₂/CO (from 1.5 to 1), 10% increase of reforming efficiency (η), 25% increase of hydrogen energy yield ($E_Y(H_2)$), and 20%

increase of ratio α . Syngas ratio 1.5, which originates from reaction (1), is achieved in a quartz reaction chamber at the two times higher air flow than required by partial oxidation reaction (1) stoichiometry.

CONCLUSIONS

Research showed that ethanol added into the reaction chamber caused the vanishing of the NO bands from the emission spectra of the torch. Reforming in steel reaction chamber showed a 10% increase of reforming efficiency and a 20% increase of hydrogen energy yield over the reforming in a quartz reaction chamber; however, the H₂/CO ratio decreased from 1.5 during reforming in the quartz chamber to 1 during reforming in the metal chamber.

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РЕФОРМИРОВАНИЕ ЭТАНОЛА В ГИБРИДНОЙ ПЛАЗМЕННО-КАТАЛИТИЧЕСКОЙ СИСТЕМЕ

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Влияние материала реакционной камеры на гибридное плазменно-каталитическое реформирование модельного углеводорода было исследовано с помощью кварцевой и стальной реакционных камер одинакового размера. Показано, что полосы NO исчезают с эмиссионного спектра плазмы во время реформирования этанола. Реформирование этанола в стальной реакционной камере показало более высокие эффективность реформирования и энергетический выход водорода, чем в кварцевой реакционной камере.

РЕФОРМУВАННЯ ЕТАНОЛУ В ГИБРИДНІЙ ПЛАЗМОВО-КАТАЛІТИЧНІЙ СИСТЕМІ

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Вплив матеріалу реакційної камери на гібридне плазмово-каталітичне реформування модельного вуглеводню було досліджено за допомогою кварцової та сталевій реакційних камер однакового розміру. Показано, що смуги NO зникають з емісійного спектра плазми під час реформування етанолу. Реформування етанолу в сталевій реакційній камері показало вищі ефективність реформування та енергетичний вихід водню, ніж у кварцовій реакційній камері.