

PLASMA-CATALYTIC REFORMING OF RICH ETHANOL-AIR MIXTURES

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Influence of the ratio between the components of the ethanol-air mixture on the characteristics of the plasma components was investigated using optical emission spectroscopy. The vibrational population distribution of excited OH molecules during the hybrid plasma-catalytic reforming was shown to not correspond with the Boltzmann distribution.

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INTRODUCTION

Interest in the conversion of renewable hydrocarbon raw materials into the feedstock suitable as a crude oil replacement for chemical industry increased with the global shift towards sustainability at the start of the 21st century. Despite important advantages, conversion of renewable raw materials into value-added chemicals has complications, which stem from the complexity and variety of their composition. The most well-developed are indirect approaches, which first convert renewable raw materials into the syngas (a mixture of H₂, CO, and light hydrocarbons) mainly via the gasification process. Produced syngas is then used in methanol or Fischer-Tropsch synthesis to obtain the desired chemicals. Unfortunately, this pathway of renewable raw materials conversion requires high energy input and provides low product yields.

Among the alternative processes that show great potential in this area is plasma technology. Low-temperature non-thermal plasma has the advantage of being able to activate chemical processes by producing electrons, excited atoms, and excited molecules, instead of initiating the reactions via heating of the reactor. In addition, plasma has already been successfully used to produce syngas from renewable raw materials. Considering this, several recent studies examined the prospect of value-added chemicals synthesis from light hydrocarbons using plasma [1] or plasma-like conditions in rich flames [2].

This work focuses on the experimental investigation of the system for the synthesis of value-added chemicals and raw materials from renewable liquid hydrocarbon using plasma-catalytic approach to the activation of chemical reactions.

1. EXPERIMENTAL SETUP AND METHODS

Fig. 1 presents the scheme of the system for plasma catalytic reforming of liquid hydrocarbons, which is based on rotating gliding discharge. The reforming system has two connected chambers: a discharge chamber and a reaction chamber. During the experiment, food-grade ethanol was used as a model hydrocarbon and atmospheric air was used as a model oxidant. The flow of air that was needed for the reforming was divided between the discharge chamber and the reaction chamber. Part of the air was introduced into the system through the discharge chamber,

activated by a discharge and used as a source of active species for reforming initiation. Plasma-activated air was introduced into the reaction chamber as a torch through the aperture in one of the electrodes. The rest of the air was mixed with ethanol and introduced through the top of the reaction chamber. Reagents were introduced into chambers tangentially to their walls as formed rotating flows. The plasma-catalytic reforming of ethanol was conducted using cylindrical quartz reaction chamber 100 mm in height and with 36 mm internal diameter. The discharge was ignited between the internal T-shaped stainless-steel anode electrode, which diameter was 25 mm, and the external grounded stainless-steel ring cathode with a 20 mm wide circular aperture in its center.

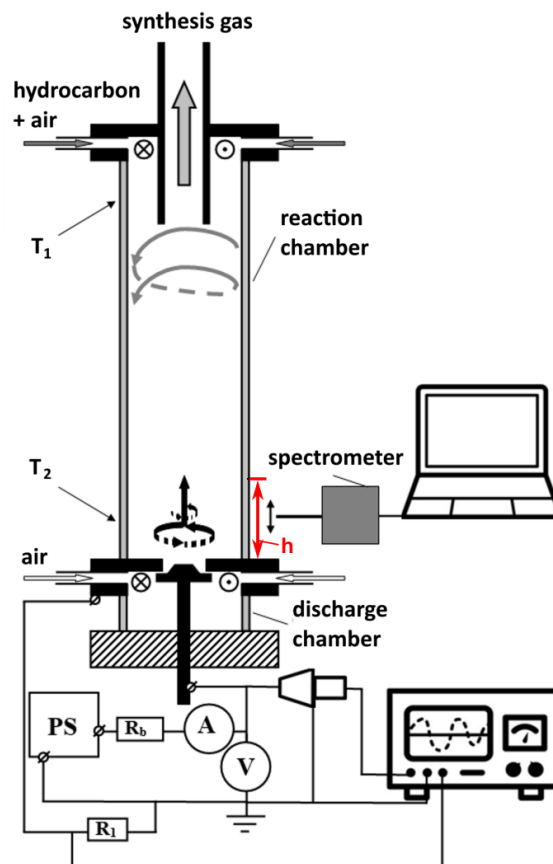


Fig. 1. Scheme of the hybrid plasma-catalytic system with rotating gliding discharge for the reforming of liquid hydrocarbons into synthesis gas

The rotating gliding discharge was powered by BP-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.

Optical emission spectroscopy (OES) of the plasma torch radiation in the quartz reaction chamber was conducted using a system consisting of an optical fiber, Solar TII (S-150-2-3648 USB) spectral device and a PC. Spectrometer operated in a wavelength range from 200 to 1000 nm. PC was used for controlling measurements and processing data obtained from the spectrometer. Spectra were measured at distance h from the discharge chamber. OES was conducted at several distances h : 0, 2.5, 5, and 7.5 mm. Optical emission spectra were used to determine the vibrational and rotational temperatures of excited hydroxyl (OH) molecules in different zones of the reforming reactor.

Reaction chamber wall 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 reaction chamber input and reaction zone, respectively.

The flows of introduced ethanol were 324, 648, and 810 ml·h⁻¹. The ratios between the introduced ethanol and oxygen were 1:1, 2:1, and 5:2, which correspond to rich mixtures with fuel-air equivalence ratios of 3, 6, and 7.5 respectively. During the study, input air flow was 10 l·min⁻¹, which at 2:1 ratio between introduced ethanol and oxygen corresponded to the stoichiometry of ethanol partial oxidation reaction.

The air flow introduced inside the discharge chamber was equal 6 l·min⁻¹ and the air flow that was mixed with ethanol and introduced inside the reaction chamber was 4 l·min⁻¹. Based on the bottom thermocouple measurements, the temperature the reaction chamber wall during reforming ranged from 200 to 300 °C. The photographs of the system during its operation were done using a Nikon™ D7100 camera.

2. RESULTS AND THEIR DISCUSSION

The discharge current during the reforming was set to 60 mA. Discharge voltage was oscillating between 600 and 800 V. Average discharge power during the reforming was approximately 45 W.

Fig. 2 shows the photographs of the reforming system in operation.

OES was conducted at $T_1 \approx 150$ °C and $T_2 \approx 250$ °C. The 100 °C difference between temperatures is due to the low thermal conductivity of the reaction chamber material – quartz.

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 810 ml·h⁻¹ ethanol flow.

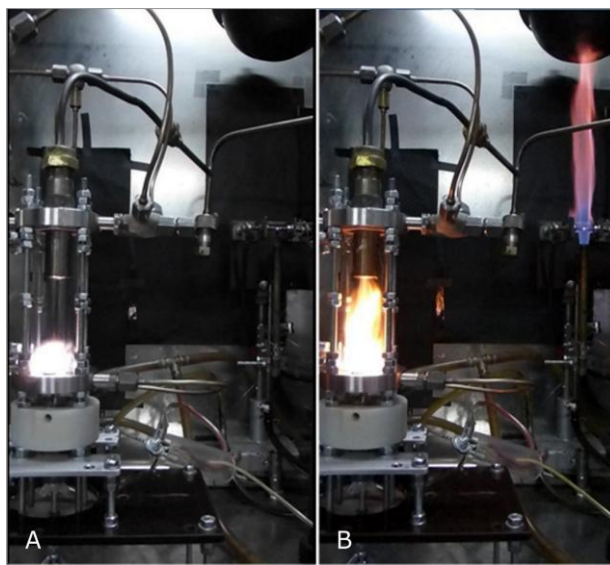


Fig. 2. Photographs of the system operating (A) only with discharge and (B) during ethanol reforming

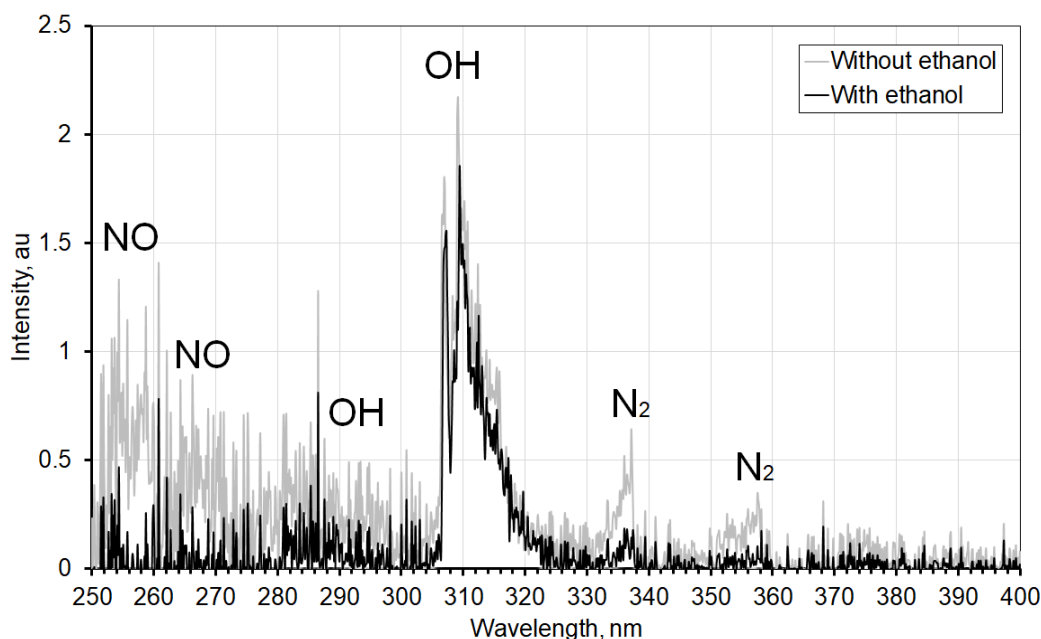


Fig. 3. Normalized emission spectra from reaction chamber at $h = 0$ mm during operation at 10 l·min⁻¹ airflow without ethanol flow (grey) and with 810 ml·h⁻¹ ethanol flow (black) ($I = 60$ mA, $U = 0.7$ kV)

Both displayed spectra (see Fig. 3) are normalized. In case of air without ethanol, the emission spectra contain bands of hydroxyl OH, nitrogen monoxide NO and low-intensity bands of nitrogen N₂. The introduction of 96 % ethanol (810 ml·h⁻¹) led to the significant decrease of the intensities of NO bands in the emission spectra and a slight decrease in the intensities of N₂ bands. The intensity drop of NO bands could appear as a response to the start of H₂ production after the introduction of ethanol, which reduces NO.

The spectra show that relative intensity of OH band in 280...300 nm wavelength range in comparison to the intensity of OH band in 300...320 nm wavelength range decreased with the introduction of ethanol. This drop of OH band intensity is caused either by the decrease of NO bands intensity that can overlap with OH bands in this wavelength range or by the decreased amount of vibrationally excited OH molecules inside the reaction chamber during the reforming of ethanol.

Obtained optical emission spectra were used to determine the temperatures that characterize the distributions of vibrational and rotational populations of excited molecules that are present in plasma. Temperatures were determined by importing the experimental spectra into Specair software [3] and

compared with the spectra that were modeled for specific vibrational and rotational temperatures of studied plasma species. Hydroxyl bands were used to obtain the desired temperatures due to their higher intensity in comparison to other species that have their bands visible on the obtained spectra.

During the fitting of spectra, shapes of the experimentally obtained OH bands located between 280 and 300 nm, which correspond to OH(A-X)(1.0), OH(A-X)(2.1), and OH(A-X)(3.2) transitions and depend on the vibrational temperature of OH, did not fit with the shapes of modeled OH spectra in this wavelength range. The comparison is presented in Fig. 4.

The lower intensity of OH(1.0) in comparison to OH(2.1) in the experimental spectra is different from the shape of modeled spectra. The difference can be caused by the non-Boltzmann distribution of the vibrational population of excited OH molecules during the reforming.

Fig. 5,a shows the rotational temperatures of hydroxyl molecules determined from the optical emission spectra measured during the reforming of 324 ml·h⁻¹ ethanol flow at different distances h from the discharge chamber.

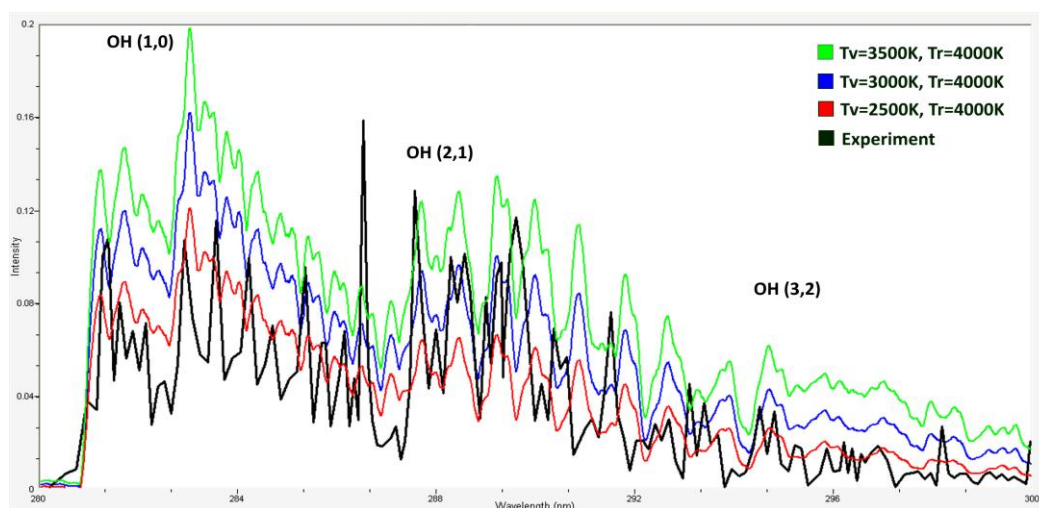


Fig. 4. Comparison between shape of experimental emission spectrum of hydroxyl (OH) and modeled spectra for different vibrational temperatures of OH, experimental spectrum obtained for 10 l·min⁻¹ airflow and 324 ml·h⁻¹ ethanol flow ($I = 60$ mA, $U = 0.7$ kV)

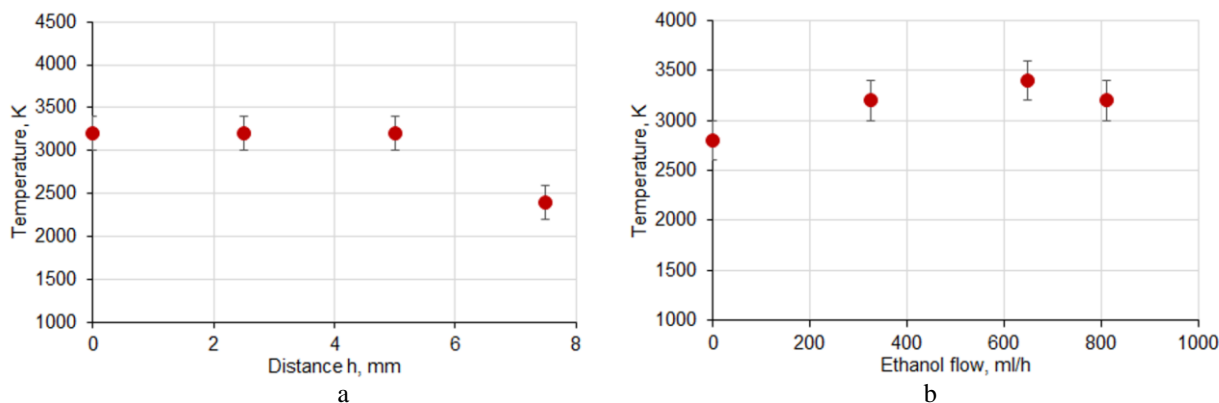


Fig. 5. Rotational (T_r) temperatures of hydroxyl (OH) during reforming determined from OES at different distances h , 10 l·min⁻¹ airflow and 324 ml·h⁻¹ ethanol flow ($I = 60$ mA, $U = 0.7$ kV) (a); rotational (T_r) temperatures of hydroxyl (OH) determined at $h = 0$ mm, 10 l·min⁻¹ airflow and different ethanol flows ($I = 60$ mA, $U = 0.7$ kV); ethanol flow 0 corresponds to OH temperatures in RGD without reforming (b)

Temperatures were compared for four different distances h : 0, 2.5, 5, and 7.5 mm. Obtained temperatures show that for h ranging from 0 to 5 mm during the plasma-catalytic reforming of ethanol rotational temperatures of hydroxyl remained almost unchanged: $T_r(\text{OH}) = (3200 \pm 200)$ K. At $h = 7.5$ mm rotational temperature of hydroxyl molecules dropped to (2400 ± 400) K. Higher temperature error margins at $h = 7.5$ mm stem from lower signal-to-noise ratio in spectra obtained at this distance.

Fig. 5,b shows the change of the rotational temperatures of hydroxyl species at different ethanol flows at distance $h = 0$ mm.

Ethanol flows that were used for the comparison were 0, 324, 648, and 810 $\text{ml} \cdot \text{h}^{-1}$. Supplied air flow was 10 $\text{l} \cdot \text{min}^{-1}$. 0 $\text{ml} \cdot \text{h}^{-1}$ ethanol flow corresponded to the operation of discharge without ethanol supply and reforming.

At 0 $\text{ml} \cdot \text{h}^{-1}$, the vibrational temperature of hydroxyl was (4000 ± 200) K, which was higher than the rotational temperature $((2800 \pm 200)$ K). These temperatures indicate that rotating gliding discharge produced non-equilibrium plasma. The addition of ethanol flow (324 $\text{ml} \cdot \text{h}^{-1}$) and initiation of the reforming led to the rise of the rotational temperature of OH to (3200 ± 200) K; however, as was previously mentioned, the determination of vibrational temperature during the reforming was impossible due to the shape difference between the modeled and experimental spectra. With the increase of the ethanol flow to 648 $\text{ml} \cdot \text{h}^{-1}$ rotational temperature of excited OH molecules slightly increased to (3400 ± 200) K and at 810 $\text{ml} \cdot \text{h}^{-1}$ ethanol flow rotational temperature of OH was (3200 ± 200) K.

Obtained data shows that the increase of the ethanol flow at the same airflow has little effect on the rotational temperature of OH molecules near the reaction zone, which remains the same within the error margin of the used temperature measurement method. At the same time, the shape of experimental spectra indicates the non-Boltzmann distribution of the vibrational population of excited OH molecules during the hybrid plasma-catalytic reforming of ethanol. The shift from the Boltzmann distribution observed during the discharge operation without reforming can be caused by the active role of the energy of vibrationally

excited molecules in the reforming reactions. This differentiates hybrid plasma-catalytic reforming from the situation during the direct injection of ethanol into the discharge chamber [4]. In that case, the vibrational temperature of excited OH molecules remained unchanged while their rotational temperature increased with the increase of ethanol flow.

CONCLUSIONS

Research showed that during plasma-catalytic reforming of rich ethanol-air mixtures the vibrational population distribution of OH does not correspond to Boltzmann distribution. The deviation from the Boltzmann vibrational population distribution may indicate the active role of the vibrationally excited OH molecules in the reforming reactions. The influence of the specific vibrational energy levels of OH on the reforming process requires further investigation via experiments and numerical simulation of reforming kinetics.

Reforming leads to a slight increase of OH rotational temperature when compared to the operation of rotating gliding discharge. In the experimental setup, rotational temperature remains stable alongside the axis of the reaction chamber for h ranging from 0 to 7.5 mm. The increase of fuel-air equivalence ratio has little impact on the rotational temperature of excited OH molecules.

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ПЛАЗМЕННО-КАТАЛИТИЧЕСКОЕ РЕФОРМИРОВАНИЕ ОБОГАЩЕННЫХ ЭТАНОЛ-ВОЗДУШНЫХ СМЕСЕЙ

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Влияние соотношения между компонентами этанол-воздушной смеси на характеристики компонент плазмы было исследовано с помощью оптической эмиссионной спектроскопии. Показано, что во время реформирования распределение заселения колебательных уровней возбужденных молекул OH не соответствует распределению Больцмана.

ПЛАЗМОВО-КАТАЛІТИЧНЕ РЕФОРМУВАННЯ ЗБАГАЧЕНИХ ЕТАНОЛ-ПОВІТРЯНИХ СУМІШЕЙ

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Вплив співвідношення між компонентами суміші етанол-повітря на характеристики компонент плазми було досліджено за допомогою оптичної емісійної спектроскопії. Показано, що під час реформування розподіл заселення коливних рівнів збуджених молекул OH не відповідає розподілу Больцмана.