

# ETHANOL REFORMING IN PLASMA-LIQUID SYSTEM WITH POSTDISCHARGE HIGHEMPERATURE PYROLITIC CHAMBER

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Plasma assist high temperature partial oxidation pyrolysis of ethanol was investigated. The energy efficiency vs. pyrolysis chamber temperature and vs. ethanol-to-oxygen molar rate was obtained. The best regimes for highest energy efficiency were obtained. The outflow syngas components were investigated.

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## 1. INTRODUCTION

From physics and chemistry of fuel combustion it is known that addition of light inflammable gases ( $H_2$ ,  $CO$ ) essentially improves ignition/combustion of heavy oil and bio-fuels [1]. Therefore hydrogen is considered as one of the most prospective energy sources for the future that can be renewable, ecologically clean and environmentally safe [2]. Among possible technologies for free hydrogen production, including steam reforming and partial oxidation of bio-fuels [3], a low-temperature plasma-assisted fuel reforming is believed to be a good alternative approach [4,5]. Also the use of fuel reforming can solving two basic tasks: the presence of quickly combustible fuel on board of aircraft and the maintenance of cooling of aircraft systems. The possible approach to the decision of these tasks can be on-board reforming of fuel (for example, kerosene), i.e. its conversion into  $H_2$  and  $CO_2$ : hydrogen can be used for combustion and carbon dioxide - for aircraft cooling purposes.

For plasma fuel reforming, various methods using thermal and non-thermal plasma are known [6]. Thermal plasma, which is thermodynamically equilibrium, has characteristics of high ionization by higher energetic density. This has merits of good rate of fuel decomposition but demerits of poor chemical selectivity and high specific energy consumption. Non-thermal (low-temperature) plasma, which is kinetically non-equilibrium, has characteristics of low ionization but benefits of high reactivity and selectivity of chemical transformations providing high enough productivity at relatively low energy consumption; this can be obtained by high voltage discharge in a flow at low or high atmospheric pressures [7, 8]. The reforming output - syngas is an important intermediate for various synthesizing chemicals and green fuels. Better way for syngas obtaining with help of plasma is using plasma system with postdischarge pyrolytic chamber, but different reforming processes (dry reforming, partial oxidation, steam reforming) produce different  $H_2/CO$  molar ratios which is very important for synthesis procedure.

For reforming with plasma support it is preferable to utilize the high plasma flow rate generators: the pulsed systems and systems on the base of TORNADO discharge type [9] etc. Thus, in work ethanol reformation at high temperature partial oxidation pyrolysis with pulsed plasma assist was investigated.

## 2. EXPERIMENTAL SETUP AND ANALYSE METHODS

The pyrolysis of ethanol after initial plasma-assisted ethanol reforming was studied by using the pulse DGCLW. The unit with pulse DGCLW is shown in Fig. 1.

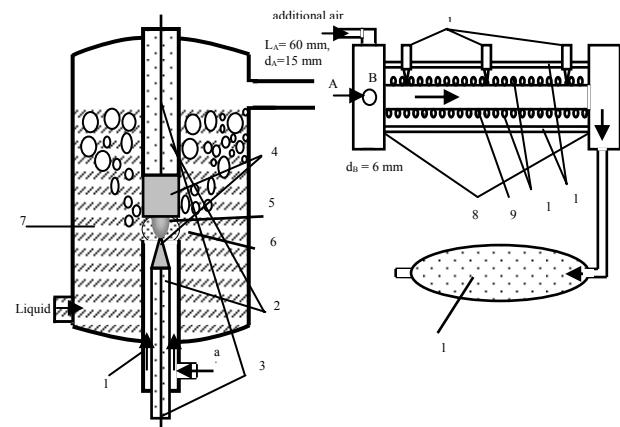


Fig. 1. Schematic of ethanol pyrolysis after plasma-assisted reforming of ethanol in the DGCLW

The installation consists of two main parts: 1) electric discharge plasma reactor, which generates a pulsed discharge in gas channel with liquid ethanol, and 2) pyrolytic reactor, which treats ethanol-air vapours mixed with products generated by plasma reactor, where (1) is a Teflon insulator around the steel pins, (2) are steel pins through which voltage is applied, (3) are copper electrodes, conical bottom and top cylinder, (4) is a discharge plasma zone between electrodes, (5) is a bubble between electrodes, (6) is a bubbling zone in the liquid, (7) is a work liquid (solution of 96% pure ethanol and distilled water), (8) are mixing inlet and outlet chamber, (9) is a steel pyrolytic chamber; (10) are electric heaters, (11) is a casing; (12) are thermocouples for temperature control, (13) is a glass vessel (0.5 l) for syngas collection. For gas analyse gas chromatography (GS) by chromatograph 6890 N Agilent and massspectrography (MS) by monopolistic mass-spectrometer MX 7301 methods were used.

## 3. RESULTS

Typical voltage and current oscillogrammes presented in Fig. 2. There you can see that discharge current was about hundreds of Ampere when voltage was about thousand Volts and pulse duration was about few microseconds.

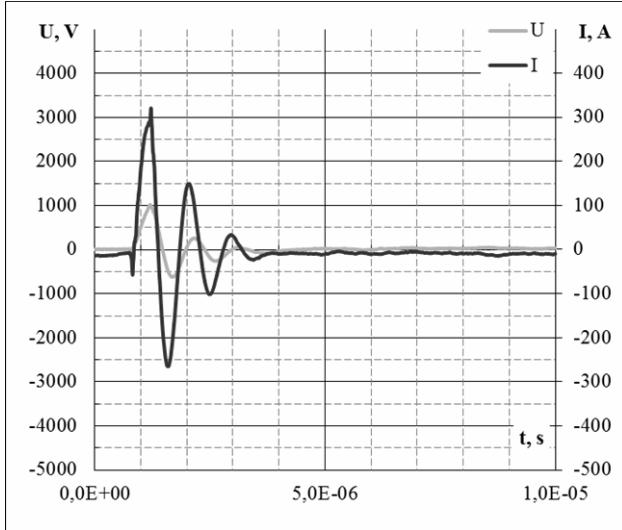


Fig. 2. Discharge current and voltage oscillogrammes

The ethanol postdischarge pyrolysis studies results after initial plasma-assisted ethanol reforming are presented in Figs. 3, 4. The parameters in the system were following: pulsed discharge frequency of 400 Hz, air flow rate of 17...28 cm<sup>3</sup>/s, time of treatment (measurements) up to 10 min (600 s); the temperature in the pyrolytic chamber varied from 0 to 870 K. Fig. 3 shows the H<sub>2</sub> intensity obtained by mass-spectrometry and the partial H<sub>2</sub> content in syngas products measured by gas-chromatography after the treatment. One can see a good correlation between gas chromatography and mass-spectrometry data.

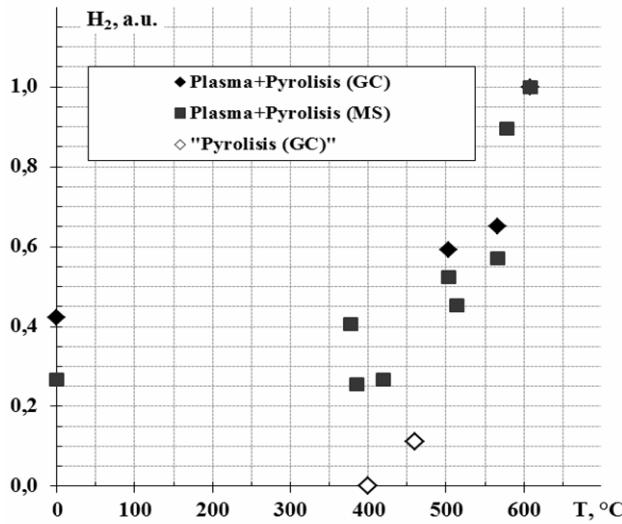


Fig. 3. H<sub>2</sub> intensity (MS) and partial H<sub>2</sub> content in syngas products (GC) after the ethanol reforming versus postdischarge pyrolytic chamber temperature

Fig. 4 shows the values of energy efficiency  $\alpha$  in the system depending on temperature in the postdischarge pyrolytic chamber. It is seen an energy efficiency increase with increasing temperature.

Some modes with the change of air flow modes (correspond to additional air supply into the pyrolytic chamber compared with an air supply in the discharge) have lower energy efficiency than the mode with a constant air flow because of varying partial output of isobutene  $i\text{C}_4\text{H}_{10}$ .

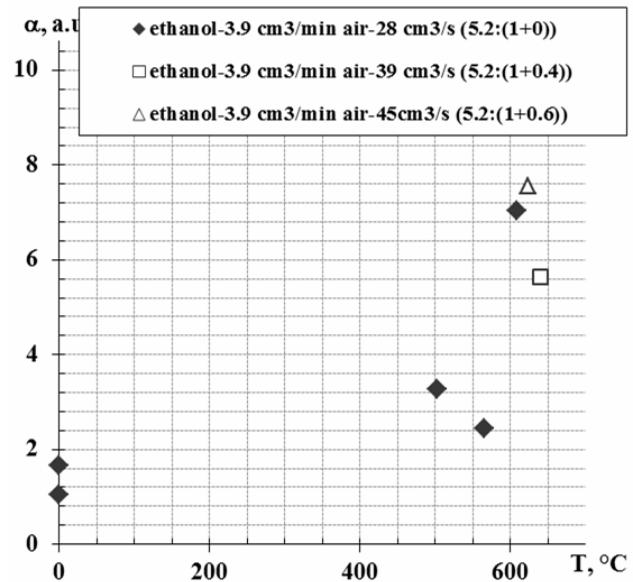


Fig. 4. Energy efficiency of ethanol reforming versus temperature in the postdischarge pyrolytic chamber

Energy efficiency calculation formula:

$$\alpha = \frac{\sum_i \text{Syngas}_i \times \text{LHV}(\text{Syngas}_i)}{\text{IPE}}$$

In this formula LHV means syngas component low heat value when IPE means electrical power for plasma. The next Fig. 5 shows the rates of syngas generation in the system. One can conclude that the investigated combination (electric discharge + postdischarge pyrolysis) reforming of ethanol demonstrates smart efficiency of this approach.

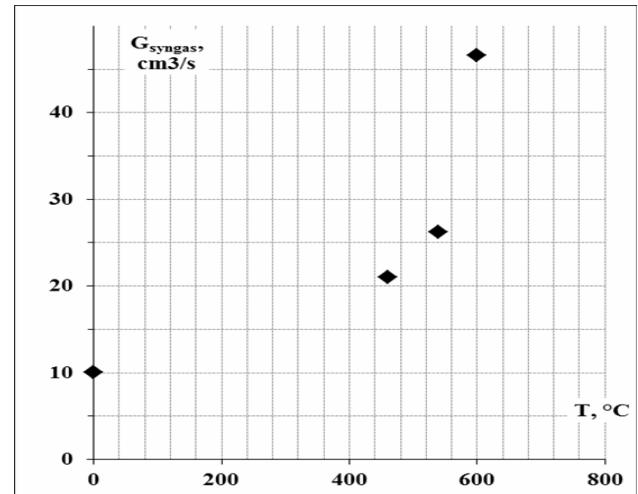
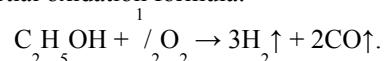


Fig. 5. The rate of syngas generation versus temperature in the pyrolytic chamber

Fig. 6 shows LHV of syngas that depends from ethanol/oxygen-in-air molar rate due to stehiometric ethanol partial oxidation formula:



So we can see the LHV enhancement when ethanol/oxygen-in-air molar rate moving to 2.

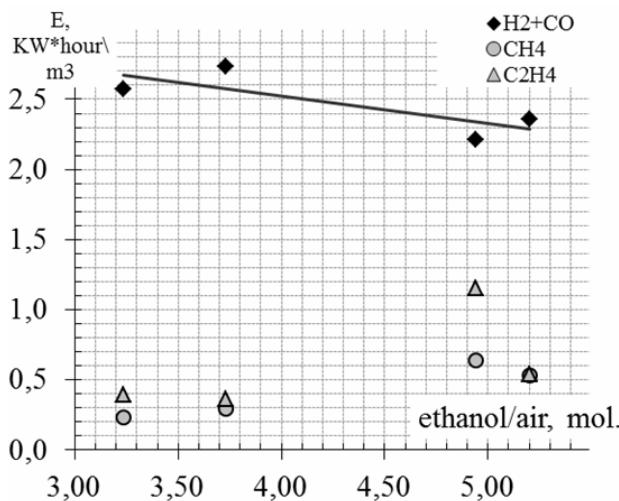


Fig. 6. Syngas components LHV versus ethanol/air molar rate

Fig. 7 demonstrates MS data of H<sub>2</sub> intensity for pulsed plasma assisted pyrolysis and only pyrolysis with ethanol/oxygen-in-air molar ratio 5.2:1. Pulsed plasma assist pyrolysis energy efficiency was sum of pulsed plasma ethanol reforming and only pyrolysis energy efficiencies. "D+P" markers show plasma assist pyrolysis process MS data when "P" shows only pyrolysis process MS data.

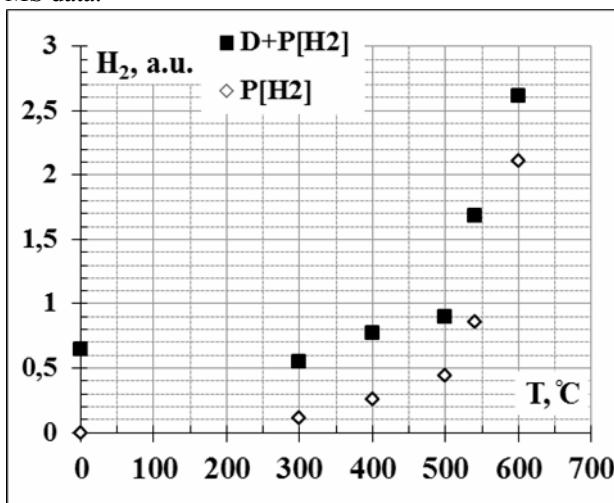


Fig. 7. H<sub>2</sub> intensity (MS) plasma reforming and partial oxidation pyrolysis versus pyrolytic chamber temperature

## 4. CONCLUSIONS

1. The use of pyrolytic chamber allowed getting the energy efficiency value more than three times higher than such value for the similar plasma-liquid systems without pyrolytic chamber.
2. Process energy efficiency was the sum of pulsed plasma reforming and hightemperature partial oxidation pyrolysis processes.
3. The best energy efficiency is observed at the maximal pyrolytic chamber (600 °C).
4. The ethanol/oxygen molar ratio increasing decreases H<sub>2</sub>+CO LHV and improves CH<sub>4</sub> LHV and C<sub>2</sub>H<sub>2</sub> LHV.

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## РЕФОРМИРОВАНИЕ ЭТАНОЛА В ПЛАЗМЕННО-ЖИДКОСТНОЙ СИСТЕМЕ С ПОСТРАЗРЯДНОЙ ВЫСОКОТЕМПЕРАТУРНОЙ ПИРОЛИТИЧЕСКОЙ КАМЕРОЙ

**C.М. Сидорук, В.Я. Черняк, С.В. Ольшевский**

Исследован высокотемпературный пиролиз частичного окисления этанола с поддержкой плазмы. Получены зависимости энергетической эффективности от температуры пиролитической камеры и от молярного соотношения этанола к воздуху в подаваемой смеси. Исследованы режимы с наивысшей энергетической эффективностью системы, а также компоненты синтез-газа на выходе системы.

## РЕФОРМУВАННЯ ЕТАНОЛУ В ПЛАЗМОВО-РІДИННІЙ СИСТЕМІ З ПОСТРАЗРЯДНОЮ ВИСОКОТЕМПЕРАТУРНОЮ ПІРОЛІТИЧНОЮ КАМЕРОЮ

**С.М. Сидорук, В.Я. Черняк, С.В. Ольшевський**

Досліджено високотемпературний піроліз часткового окислення етанолу з підтримкою плазми. Отримано залежності енергетичної ефективності від температури піролітичної камери та від молярного співвідношення етанолу до повітря в вихідній паливній суміші. Досліджено режими з найвищою енергетичною ефективністю системи, а також компоненти синтез-газу на виході системи.