

PLASMA-CATALYTIC REFORMING OF LIQUID HYDROCARBONS

*O.A. Nedybaliuk¹, V.Ya. Chernyak¹, V.V. Kolgan¹, V.V. Iukhymenko¹, O.V. Solomenko¹,
I.I. Fedirchyk¹, E.V. Martysh¹, V.P. Demchina², N.V. Klochok³, S.V. Dragnev⁴*

¹*Taras Shevchenko National University of Kyiv, Ukraine;*

²*The Gas Institute of NASU, Kyiv, Ukraine;*

³*National Technical University of Ukraine "Kyiv Polytechnic Institute", Kyiv, Ukraine;*

⁴*National University of Bioresources and Environmental Sciences of Ukraine, Kyiv, Ukraine*

E-mail: oanedybaliuk@gmail.com, chernyak_v@ukr.net

The series of experiments studying the plasma-catalytic reforming of liquid hydrocarbons was carried out. The dynamic plasma-liquid system based on a low-power rotating gliding arc with solid electrodes was used for the investigation of liquid hydrocarbons reforming process. Conversion was done via partial oxidation. A part of oxidant flow was activated by the discharge. Synthesis-gas composition was analysed by means of mass-spectrometry and gas-chromatography. A standard boiler, which operates on natural gas and LPG, was used for the burning of synthesis-gas.

PACS: 50., 52., 52.50.Dg

INTRODUCTION

Plasma chemistry of XX century considered plasma as chemically active environment, which activity is accomplished by high temperature and high concentration of active components: ions, electrons, radicals, excited particles and photons. Plasma as the source of active particles can initiate and significantly accelerate plasma-chemical transformations. The plasma-dynamic systems with the vortex [1-3] and reverse vortex [4, 5] gas flow, in contrast to the classical gas discharges, have additional factors that strongly affect plasma energy parameters. The use of dynamic plasma-liquid systems for conversion of hydrocarbon fuels into synthesis-gas is among the most promising areas of modern plasma chemistry. However, the use of plasma reforming [5, 6] of hydrocarbons is not economically viable [5] in comparison with plasma-catalytic reforming [5, 7-11]. In latter the plasma is used only as a catalyst, therefore less electric energy, which is the most expensive type of energy, is spent on plasma generation. That is why the development and investigation of new plasma systems that would work at high pressures, generate non-equilibrium plasma, and have long service life and high energy efficiency are among the top priorities of plasma chemistry.

The investigation of ethanol reforming process was conducted on the dynamic plasma system based on the low-power rotational gliding arc with solid electrodes. Discharge chamber of this dynamic system is the prototype of discharge chamber of plasma-liquid system with reverse vortex flow of tornado type, but without liquid [12, 13]. Hydrocarbon reforming was done via partial oxidation process. It is well-known that plasma reforming is based on a process where the oxidant and hydrocarbon are passed through discharge plasma. During the plasma-catalytic reforming only part of oxidizer is activated by a discharge and mixed with the hydrocarbon fuel in the pyrolytic reactor after that. This part of the oxidizer (~30%) was activated using rotational gliding arc with solid electrodes and was introduced as a plasma torch into the reaction (pyrolytic) chamber, where it interacted with the

mixture of hydrocarbon and the rest of oxidant (~70%). In addition, this approach made it possible to increase plasma derivation from equilibrium state [14].

1. EXPERIMENTAL SET-UP

Schematic view and photo of the experimental setup are shown in Fig. 1. The base of experimental setup is the cylindrical quartz discharge chamber and the metal reaction (pyrolytic) camera. The top and the bottom of quartz chamber is sealed with flanges. The top metal flange, the center of which contained a stainless steel sleeve, worked as one of the electrodes. The sleeve had a nozzle at its center and one end of the discharge glided on its surface. The second electrode was cylindrical and T-shaped. It had been introduced into the chamber through a hole in the lower flange. Both electrodes were made of stainless steel and was water-cooled to room temperature. Discharge was supplied by BP-100 DC power source, which provides a voltage of up to 7 kV. With a ballast resistor of 4...120 kOhm, the stability range of discharge current is 20...400 mA. Working gas was injected into the discharge chamber tangentially to the sidewall of quartz cylinder, forming a vortex flow. Rotating gas moved to the nozzle and entered through it into the pyrolytic chamber, forming a plasma torch. The temperature in pyrolytic chamber was maintained by the heating element in 200...900°C range. Two thermocouples were attached to the outer wall of pyrolytic chamber. The mixture of hydrocarbon and oxidant was introduced tangentially to the side wall of reaction chamber, forming a reverse vortex flow of "tornado" type. Synthesis-gas generated in the pyrolytic chamber fell into a fridge, which was water-cooled to the room temperature. Thereafter, synthesis-gas flow rate was measured by a rotameter. Next, the synthesis-gas was gathered into a flask, and its composition was analyzed using mass spectrometry and gas chromatography. Because the system can work continuously for a long time, produced synthesis-gas was burned as a safety precaution against its accumulation. The synthesis-gas was burned in a standard boiler by NAVIEN that normally operates on natural gas and LPG.

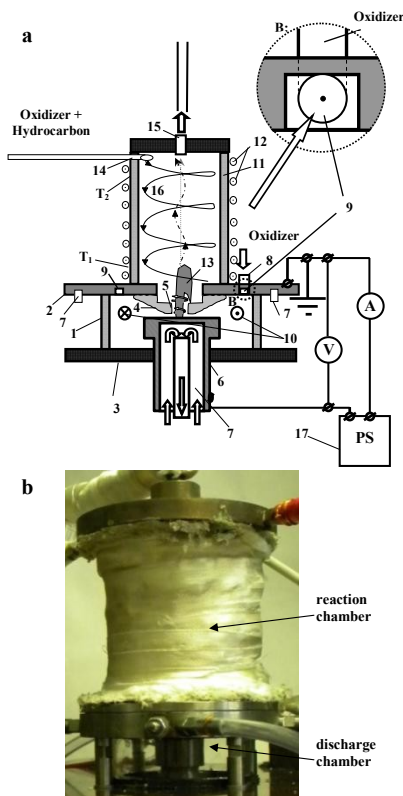
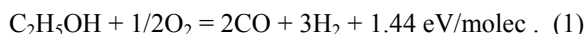


Fig. 1. Schematic (a) and photo (b) of experimental setup: 1 – quartz chamber; 2,3 – flanges; 4,5 – sleeves; 6 – T-shaped electrode; 7 – water cooling; 8 – oxidizer inlet; 9 – directional pipe; 10 – gas flow direction; 11 – pyrolytic chamber; 12 – heater; 13 – plasma torch; 14 – hydrocarbon inlet; 15 – reforming products outlet; 16 – gas flow direction; 17 – power source

Ethanol (C_2H_5OH) was used as a model hydrocarbon and air oxygen - as a model oxidant. The flows of air and ethanol were chosen correspondingly to the stoichiometry of partial oxidation reaction:



During all plasma-catalytic reforming test modes the highest wall temperature of pyrolytic chamber was maintained at $(450 \pm 10)^\circ C$, the discharge current was 60 mA and near 30% of airflow was blown through the discharge. Additional research of plasma-catalytic reforming of diesel fuel of petroleum origin and vegetable oil, from which biodiesel is produced, was carried out.

2. RESULTS AND DISCUSSION

Fig. 2,a shows the dependence of discharge voltage U_d on the amount of air flow through the discharge with $I_d = 60 \text{ mA}$. Power, which was introduced in the discharge, increased as an air flow raised in the range of $(0..4 \text{ L}\cdot\text{min}^{-1})$. However, the power put into the discharge has not changed when airflow was between $5 \text{ L}\cdot\text{min}^{-1}$ and $8 \text{ L}\cdot\text{min}^{-1}$. Fig. 2,b shows the air flow into the system and the synthesis-gas flow out of the system as the functions of power which is delivered by C_2H_5OH into the pyrolytic chamber. There was no C_2H_5OH reforming when discharge was turned, it evaporated in the pyrolytic chamber, and subsequently condensed in a

refrigerator. Synthesis-gas flow increased linearly with the increase of power delivered by C_2H_5OH .

The results of gas chromatography of gaseous products of C_2H_5OH reforming are shown in Fig. 3. The composition of gas mixture does not depend on the amount of converted ethanol.

The data about the synthesis-gas flow at the outlet, its composition and density of electrical energy required for the plasma-catalytic reforming, was used to calculate the electrical energy transformation coefficient – α and the conversion efficiency – η :

$$\alpha = \frac{Q_s}{Q_p}, \quad \eta = \frac{Q_s}{Q_{C_2H_5OH}} \times 100\% \quad (2)$$

where Q_s – heat energy released by the complete combustion of synthesis-gas, Q_p – the electrical energy necessary for supporting reforming, $Q_{C_2H_5OH}$ – thermal energy released by the complete combustion of C_2H_5OH .

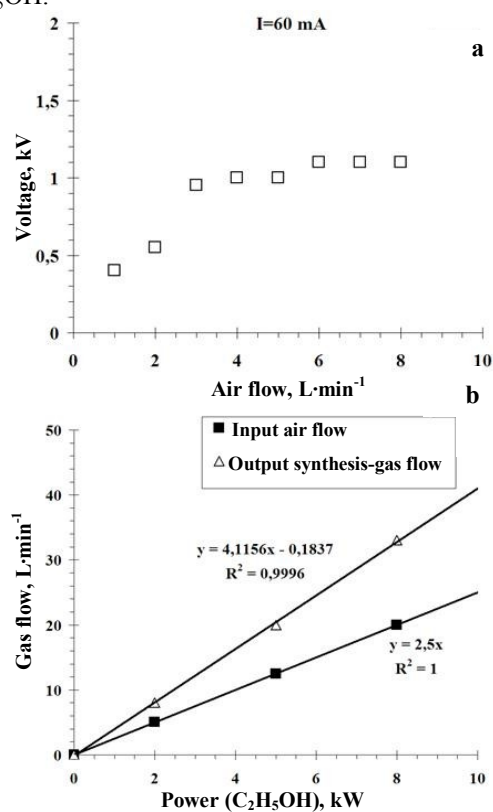


Fig. 2. Voltage in discharge gap as function of air flow (a); input air flow and output synthesis-gas flow as functions of power delivered by C_2H_5OH into pyrolytic chamber (b)

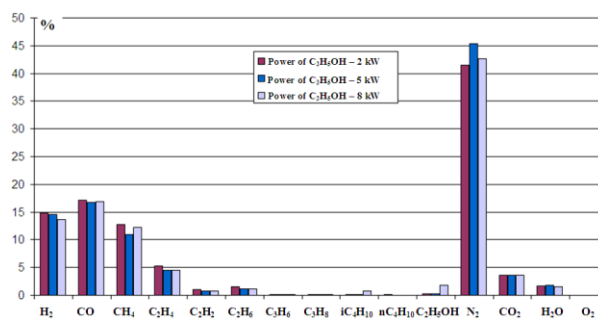
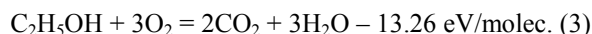


Fig. 3. Results of gas-chromatography of synthesis-gas

C₂H₅OH conversion efficiency during this experiment was higher than 80%. Fig. 4,a shows the electrical energy transformation coefficient (α) as function of power which is delivered by C₂H₅OH into the pyrolytic chamber. Fig. 4,b shows: the calculated power of combustion of synthesis-gas produced by the reforming reaction (1); the power of synthesis-gas combustion, based on the results of gas chromatography and the value of synthesis-gas flow (see Fig. 2,b); the power of C₂H₅OH combustion, in an assumption that CO₂ presented at the output of system was formed with the full ethanol combustion as the functions of power which is delivered by C₂H₅OH into the pyrolysis chamber:



The reactor temperature of $(450 \pm 10)^\circ\text{C}$ is substantially lower (by approximately 50%) in comparison with a conventional pyrolysis. The electric energy transformation coefficient of presented system for plasma-catalytic reforming of liquid hydrocarbons into synthesis-gas is several tens times higher ($\alpha \approx 90$ for C₂H₅OH) than in plasma reforming systems ($\alpha \approx 0.8$ [15-17], $\alpha \approx 1.5$ [18, 19], $\alpha \approx 2$ [6]) and two times higher than in well-known analogues ($\alpha \approx 30..40$ [5]). As mentioned before, produced synthesis-gas was burned in the boiler to prevent its accumulation. Fig. 5 shows the photos of synthesis-gas flame.

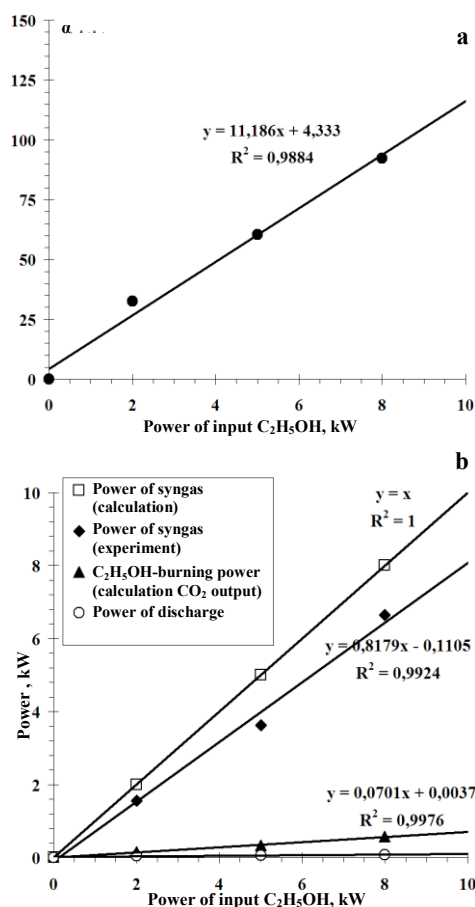


Fig. 4. Electric energy transformation coefficient α (a), power of synthesis-gas combustion, power of synthesis-gas combustion, and power of ethanol combustion as functions of power which is delivered by C₂H₅OH into the chamber (b)

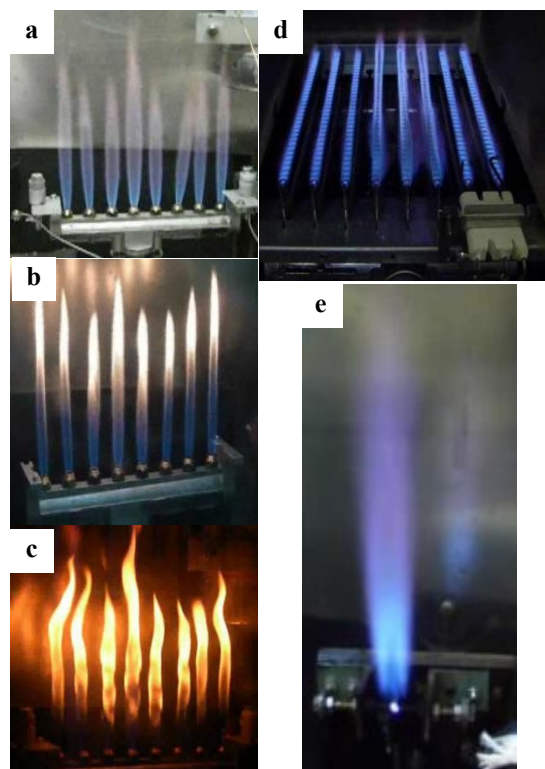


Fig. 5. Photos of flame: a – synthesis-gas (5 kW) from C₂H₅OH; b – synthesis-gas (5 kW) produced from vegetable oil that is used for biodiesel production; c – synthesis-gas (5 kW) produced from diesel fuel of petroleum origin; d – synthesis-gas (10 kW) produced from C₂H₅OH, burning in the standard boiler; e – combustion of synthesis-gas (10 kW) produced from C₂H₅OH via transverse arc (50 W)

The flame of synthesis-gas produced from the vegetable oil was more stable and had much lower content of carbon black than the flame of diesel fuel. Synthesis-gas flame from C₂H₅OH had blue color and temperature of 1050...1100°C. Synthesis-gas is effectively burned by the standard boiler, which is designed to operate on natural gas and LPG.

CONCLUSIONS

Research of the scheme of plasma-catalytic reforming of liquid hydrocarbons into synthesis-gas, proposed in this paper, showed that its electric energy transformation coefficient is several tens times higher ($\alpha \approx 90$) than in plasma reforming ($\alpha \approx 2$ [6]) and two times higher than in well-known analogues ($\alpha \approx 30..40$ [5]); reactor temperature is substantially less (by approximately 50%) when comparing with conventional pyrolysis; synthesis-gas component composition stays almost unchanged and C₂H₅OH conversion efficiency is $\geq 80\%$ in the tested power range; the synthesis-gas is effectively burned by the NAVIEN boiler, which is designed to operate on natural gas and LPG.

ACKNOWLEDGEMENTS

This work was partially supported by the Ministry of Education and Science of Ukraine, National Academy of Sciences of Ukraine, Taras Shevchenko National University of Kyiv.

REFERENCES

1. A.S. Koroteev, V.M. Mironov, Yu.S. Svirchik. *Plasmatrons: constructions, characteristics, calculation*. M., 1993, 286 p.
2. V. Chernyak. Gas discharge plasma in dynamics system as a nonequilibrium plasma sources // *Proc. 3rd Czech-Russian Seminar on Electrophysical and Thermophysical Processes in Low-temperature Plasma, Brno, November 16-19. 1999*, p. 94-99.
3. J.M. Cormier, I. Rusu, A. Khacef. On the use of a magnetic blow out glidarc reactor for the syngas production by stem reforming // *16th International symposium on plasma chemistry, Taormina. 2003*.
4. C.S. Kalra, M. Kossitsyn, K. Iskenderova, A. Chirokov, Y.I. Cho, A. Gutsol, A. Fridman. Electrical discharges in the reverse vortex flow – tornado discharges // *El. Proc. Of 16th Int. Symp. on Plasma Chem. Taormina. 2003*.
5. A. Fridman. *Plasma chemistry* // Cambridge University Press, New York. 2008. www.cambridge.org/9780521847353
6. V.I. Arkhipenko, S.M. Zgirouski, A.G. Karoza, et al. Diagnostics of ethanol conversion products by IR absorption spectroscopy // *Journ Appl. Spectroscopy. 2013*, v. 80, № 1, p. 99-103.
7. A. Czernichowski, K. Wesolowska. *Generation of the sintesis gas from bioethanol*: Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem. 2006, v. 51, № 2.
8. A. Czernichowski, M. Czernichowski, K. Wesolowska // *2nd Int. Conference on Fuel Cell Science, Engineering and Technology, Rochester, New York. 2004*, p. 75.
9. L. Bromberg, D.R. Cohn, K. Hadidi, J. Heywood, A. Rabinovich. Diesel engine emission reduction (DEER) // *Workshop, Coronado, CA. 2004*.
10. C.S. Kalra. Gliding arc in tornado and its application for plasma-catalytic partial oxidation of methane // *Thesis, Drexel University, Philadelphia, PA. 2004*.
11. C.S. Kalra, A.F. Gutsol, A.A. Fridman. Gliding arc discharges as a source of intermediate plasma for methane partial oxidation // *IEEE Trans. Plasma Sci. (33). 2005*, № 1, p. 32-41.
12. O.A. Nedybaliuk, V. Ya. Chernyak, S.V. Olszewski. Plasma-liquid system with reverse vortex flow of “tornado” type (TORNADO-LE) // *Problems of Atomic Science and Technology. Series “Plasma Physics” (16). 2010*, № 6, p. 135-137.
13. O.A. Nedybaliuk, V.Ya. Chernyak, et al. Dynamic plasma-liquid system with discharge in reverse vortex flow of “tornado” type // *International Journal of Plasma Environmental Science and Technology (5). 2011*, № 1, p. 20-24.
14. V. Chernyak, V. Iukhymenko, I. Prysiazhnevych, and Eu. Martysh. The influence of exothermic reactions on the nonequilibrium level of discharge plasma // *Problems of Atomic Science and Technology (8). 2013*, № 4, p. 200-203.
15. D.S. Levko et al. Obtaining molecular hydrogen in electric discharge of the tornado type in air mixture with ethanol and water vapors // *Technical Physics Letters. 2010*, v. 36, № 11, p. 998-1000.
16. V.Ya. Chernyak et al. Reforming of simple hydrocarbons in plasma liquid systems // *19th Symposium on Physics of Switching Arc, Brno, Czech Republic, 5-9 September. 2011*, p. 17-26.
17. Chernyak, O. Nedybaliuk, E. Martysh, et al. Plasma reforming of liquid hydrocarbon in plasma-liquid systems // *Nukleonika. 2012*, v. 57, № 2, p. 301-305.
18. O.A. Nedybaliuk, O.I.V. Solomenko, V.Ya. Chernyak, et al. Reforming of bioethanol in the system with reverse vortex air/CO₂ flow of “tornado” type with liquid electrode // *Problems of Atomic Science and Technology. 2012*, № 6, p. 178-180.
19. A.N. Tsybalyuk, D.S. Levko, V.Y. Chernyak, et al. Influence of the gas mixture temperature on the efficiency of synthesis gas production from ethanol in a nonequilibrium plasma // *Technical Physics. 2013*, v. 58, № 8, p. 1138-1143.

Article received 20.11.2014

ПЛАЗМЕННО-КАТАЛИТИЧЕСКОЕ РЕФОРМИРОВАНИЕ ЖИДКИХ УГЛЕВОДОРОДОВ

О.А. Недыбалюк, В.Я. Черняк, В.В. Колган, В.В. Юхименко, Е.В. Соломенко, И.И. Федирчик, Е.В. Мартыш, В.П. Демчина, Н.В. Клочок, С.В. Драгнев

Проведена серия экспериментов, изучающих плазменно-каталитическое реформирование жидких углеводородов. Динамическая плазменно-жидкостная система на основе маломощной вращательной скользящей дуги с твердыми электродами использовалась для исследования процесса реформирования жидких углеводородов. Конверсия была реализована путем частичного окисления. Часть потока окислителя активировали разрядом. Состав синтез-газа анализировался с помощью масс-спектрометрии и газовой хроматографии. Стандартный котел, который работает на природном и сжиженном газе, был использован для сжигания синтез-газа.

ПЛАЗМОВО-КАТАЛІТИЧНЕ РЕФОРМУВАННЯ РІДКИХ ВУГЛЕВОДНІВ

О.А. Недыбалюк, В.Я. Черняк, В.В. Колган, В.В. Юхименко, О.В. Соломенко, І.І. Федірчик, Є.В. Мартыш, В.П. Демчина, М.В. Клочок, С.В. Драгнев

Проведено серію експериментів, які вивчають плазмово-каталітичне реформування рідких вуглеводнів. Для дослідження процесу реформування рідких вуглеводнів використовувалася динамічна плазмово-рідинна система з обертальною ковзною дугою малої потужності з твердими електродами. Конверсія була реалізована шляхом часткового окислення. Частина потоку окисника активували розрядом. Склад синтез-газу аналізувався за допомогою мас-спектрометрії та газової хроматографії. Для спалювання синтез-газу був використаний стандартний котел, який працює на природному та зрідженому газі.