PLASMA-CATALYTIC REFORMING OF ETHANOL: INFLUENCE OF AIR ACTIVATION RATE AND REFORMING TEMPERATURE

O.A. Nedybaliuk[1], V.Ya. Chernyak[1], I.I. Fedirchyk[1], V.P. Demchina[2], V.A. Bortyshevsky[3], R.V. Korzh[3]
[1]Taras Shevchenko National University of Kyiv, Kyiv, Ukraine;
[2]The Gas Institute of National Academy of Sciences of Ukraine, Kyiv, Ukraine;
[3]Institute of Bioorganic Chemistry and Petrochemistry of National Academy of Sciences of Ukraine, Kiev, Ukraine

E-mail: oanedybaliuk@gmail.com

This paper presents the study of the influence that air activation rate and reforming temperature have on the gaseous products composition and conversion efficiency during the plasma-catalytic reforming of ethanol. The analysis of product composition showed that the conversion efficiency of ethanol has a maximum in the studied range of reforming temperatures. Researched system provided high reforming efficiency and high hydrogen energy yield at the lower temperatures than traditional conversion technologies.

PACS: 50. 52., 52.50.Dg

INTRODUCTION

In order to achieve truly sustainable economy humanity has to shift production to the renewable raw materials wherever it is possible [1]. A shift from the fossil hydrocarbons to the renewable raw materials produced from the biomass is the biggest and most essential of such transitions for reaching the goals of the sustainable development. The main technological issue that slows down widespread implementation of renewable hydrocarbons lies in the lack of the well-developed methods for the efficient conversion of the renewable hydrocarbon raw materials into the desired final or intermediate products [2]. The traditional conversion technologies, such as thermos-chemical or catalytic reforming, were developed and optimized with fossil hydrocarbons in mind, which have less complex and varied composition than renewable ones. The application of thermochemical technologies to the renewable raw materials often results in the generation of undesirable products and consumes large quantities of energy. The catalytic approaches use significantly less energy, however, they often have diminished yields and lower lifetime of the employed catalysts compared to the conversion of fossil hydrocarbons [3]. The cause of decreased catalyst performance lies in the catalyst poisoning by the impurities that are present in the raw materials. As such, catalytic conversion requires the extensive preprocessing and cleaning of the renewable raw materials.

Plasma is a chemically active environment with the high concentration of active species (ions, electrons, radicals, excited particles etc.) and can stimulate and support the long-chain chemical reactions. This effect is known in plasma chemistry as plasma catalysis [4]. The use of plasma catalysis in place of the conventional catalyst removes the possibility of the catalyst poisoning and provides additional benefits, such as short reaction times and high degree of control over the process. The experiments on the plasma-catalytic reforming showed that it can achieve high values of conversion efficiency at low energy input [5]. Despite the effectiveness of plasma-catalytic reforming systems, the impact of various reforming parameters on the conversion processes and on its efficiency remains largely unstudied.

In order to gain a better understanding of the processes during the plasma-catalytic reforming of the renewable hydrocarbons we studied the plasma-catalytic conversion of ethanol in a reforming system based on rotating gliding discharge. This paper focuses on the impact of air activation rate and reforming temperature on the composition of gaseous reforming products. The air activation rate represents the ratio of air activated in discharge chamber to the total flow of air that is introduced into the reforming system during the conversion.

1. EXPERIMENTAL SET-UP

Fig. 1 shows the simplified scheme of the experimental setup.

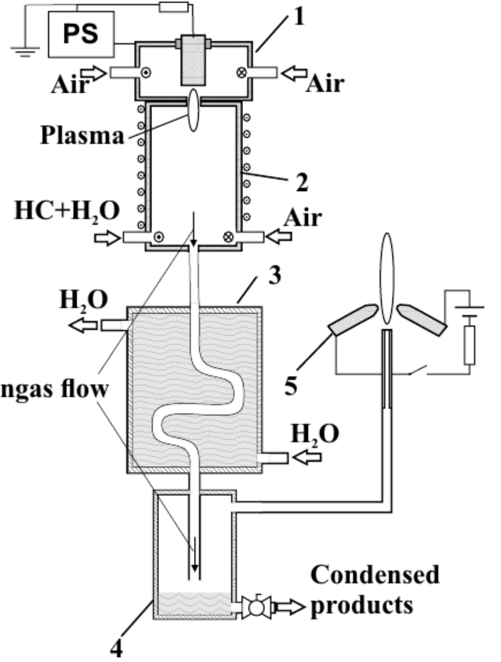

Fig.1. Schematic of experimental setup: 1 – discharge chamber; 2 – reaction chamber; 3 – cooler; 4 – condenser; 5 – combustion of produced gas

During the experiment we conducted the partial oxidation reforming of 96 % ethanol using atmospheric air. The chemical equation of partial oxidation reaction (1):

$$C_2H_5OH + 0.5O_2 = 2CO + 3H_2. \qquad (1)$$

Reforming system features two connected chambers: a discharge chamber (1) and a reaction chamber (2). The flow of air that is required for the reforming is supplied into the system by a compressor and separated between both chambers. The air injected into the discharge chamber is activated by the discharge and used as a basis for the generation of active species. The air introduced into the reaction chamber is mixed with the ethanol. Airflows in both chambers are introduced tangentially to the chamber wall. The air injection is set to create the vortex flow of air in the discharge chamber and reverse vortex flow in the reaction chamber. We controlled the air activation rate by changing the ratio between the flows of air injected into the discharge and air introduced into the reaction chamber.

The air plasma produced in the rotating gliding discharge is injected into the reaction chamber as a torch. The power introduced into the discharge ranged from 20 to 70 W. The active species in air plasma interact with the air-ethanol mixture and initiate the chain reactions of partial oxidation reforming. The temperature in the reaction chamber can be regulated by either using an external electric heater coil or by increasing the input airflows and causing the complete oxidation of ethanol in the reaction chamber. The temperature was monitored by the thermocouples attached to the top and bottom of the reaction chamber.

The products of ethanol reforming flow through a water cooler (3) that uses running tap water at room temperature. A part of the products condenses into liquid and is captured in a condenser (4). The gaseous products leave the condenser and flow towards either a sampling port or a combustion device (5). The samples of gaseous reforming products were collected in the 0.5 l glass flasks. The rest of produced gas is combusted in order to prevent its accumulation in the experimental setup.

The composition of gaseous reforming products was determined using Agilent 6890 N gas chromatograph and MX-7301 mass spectrometer. The total flow of produced gas was measured by Dwyer RMA-22-SSV and RMA-23-SSV rotameters.

2. RESULTS AND DISCUSSION

For all studied reforming modes ethanol flow into reaction chamber was 256 g/h and discharge current was set to 60 mA. The influence of the reforming temperature on the composition of gaseous reforming products was studied at reforming temperatures from 200 to 350 °C range. The air activation rate was set to 0.17, which is the minimum used in this research. The total airflow corresponded to a chemical equation (2):

$$C_2H_5OH + 0.6O_2 = 1.92CO + 2.88H_2 + \\ + 0.12H_2O + 0.08CO_2. \qquad (2)$$

The gas chromatography results for the gaseous reforming products are shown at Fig. 2.

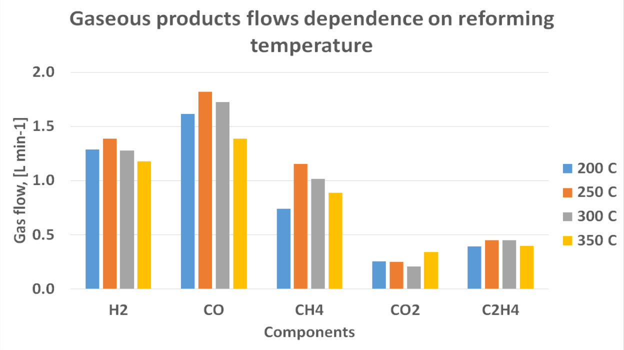

Fig. 2. Dependence of main gaseous products flows on reforming temperature

The main reforming products are hydrogen, carbon monoxide, and light hydrocarbons, such as methane and ethane.

Gas chromatography showed that the production of hydrogen, carbon monoxide and methane during reforming had a maximum at 250 °C. Obtained data on product composition allows to calculate the reforming efficiency (η) using equation (3) [6]:

$$\eta = \frac{LHV_{products} \cdot G_{progucts}}{Plasma\ power + LHV_{reactants} \cdot G_{reactants}}, \qquad (3)$$

where $LHV_{products}$ is the combined lower heating value of all gaseous reforming products with an exception of the unreacted reactants, $G_{products}$ is the total flow of gaseous reforming products, *Plasma power* is the energy input into the plasma generation, $LHV_{reactants}$ is the combined lower heating value of all reactants, $G_{reactants}$ is the total flow of reactants.

The efficiency of the reforming system in terms of hydrogen production can be evaluated from its hydrogen energy yield $E_Y(H_2)$. It corresponds to the flow of produced hydrogen $G(H_2)$ divided by the electric power spent on plasma generation *Plasma power*:

$$E_Y(H_2)\left[\frac{g}{kWh}\right] = \frac{G(H_2)\left[\frac{g}{h}\right]}{Plasma\ power\ [kW]}. \qquad (4)$$

The *Plasma power* was 30 W at 200 °C and 24 W at 250, 300 and 350 °C. The values of H_2/CO ratio, conversion efficiency and hydrogen energy yield during the conversion at different reforming temperatures are presented in Table 1.

Table 1

Reforming characteristics at different reforming temperatures at 0.17 air activation rate

Reforming temperature, [°C]	200	250	300	350
H_2/CO ratio	0.8	0.75	0.74	0.85
η, [%]	72	90	84	81
$E_Y(H_2)$, [g/kWh]	230	350	285	265

The highest conversion efficiency observed during the experiment was 90 % when the reforming temperature was maintained at 250 °C. Such conversion efficiency is comparable to the value during the ethanol conversion at the optimal regimes of catalytic partial oxidation and during the thermochemical reforming. The reforming temperature is two times lower than the common temperature used for the catalytic partial oxidation (approx. 500 °C [7]) and almost three times lower than the lower limit of the temperature used for the thermochemical reforming (> 700 °C [8]).

The H_2/CO ratio of the gaseous reforming products depends on the reforming temperature and was in range from 0.74 to 0.85.

We studied the influence of the air activation rate on the composition of reforming products and reforming efficiency by keeping the reaction chamber at constant temperature and changing the ratio between the flows of air injected into the discharge chamber and air injected into the reaction chamber. The air activation rates were 0.17, 0.21, 0.5, and 0.61. Reforming temperature was maintained at 250 °C.

The flows of different gaseous reforming products at studied air activation rates are shown at Fig. 3.

Gas chromatography data showed that the increase of air activation rate has small impact on the hydrogen yield, which remains almost constant. The increase of air activation rate from 0.17 to 0.61 leads to the decrease of carbon monoxide yield by approx. 20 % and the reduction of methane yield by approx. 50 %. The increase of carbon dioxide flow at higher air activation rates can imply the increased occurrence of complete oxidation reactions during reforming.

The change of the ratio between the air flows through the discharge and reaction chambers controlled the air activation rate. However, the increase of flow through discharge gap caused the rise of voltage needed to maintain the rotating gliding discharge, which resulted in the increase of *Plasma power*. The *Plasma power* and reforming characteristics at the different air activation rates are shown at Table 2.

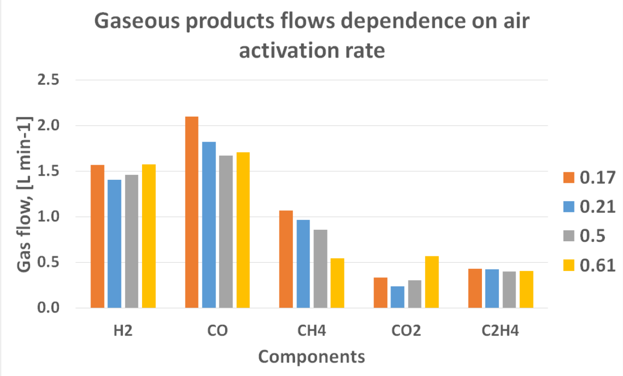

Fig. 3. Dependence of main gaseous products flows on air activation rate

Table 2

Reforming characteristics at different air activation rates at 250 °C reforming temperature

Air activation rate	0.17	0.21	0.5	0.61
Plasma power, [W]	24	24	60	48
H_2/CO ratio	0.75	0.77	0.87	0.92
η, [%]	90	86	79	73
$E_Y(H_2)$, [g/kWh]	350	315	130	175

The data shows that the increase of air activation rate leads to the increase of H_2/CO ratio in the gaseous reforming products. While the yield of hydrogen remains approximately the same, the yield of carbon monoxide and light hydrocarbons decreases with the increase of air activation rate. This, in addition to the increased value of *Plasma power*, causes the decrease of reforming efficiency from 90 % at 0.17 air activation rate to 73 % at 0.61 air activation rate.

The highest values of reforming efficiency and hydrogen energy yield in the different systems for the plasma-assisted reforming of ethanol are presented in Table 3.

Table 3

Reforming efficiency and hydrogen energy yield in different systems for plasma-assisted conversion of ethanol

Plasma source	Reaction	η, [%]	$E_Y(H_2)$, [g/kWh]
Laval nozzle arc [9]	Partial oxidation	<90	200
Dielectric barrier discharge [10]	Dry reforming	>95	6.7
Microwave discharge (2.45 GHz) [11]–[13]	Pyrolysis	~99	0.55
Microwave discharge [14]	Pyrolysis	~100	14.8
Arc discharge [15]	Partial oxidation	<65	120
GEN3 [16], [17]	Partial oxidation	<70	144
Dielectric barrier discharge [10]	Steam reforming	100	13.3
Rotating gliding discharge (this work)	Partial oxidation	90	350

The data presented in Table 1 shows that the plasma-catalytic reforming system studied in this work shows both high reforming efficiency and high hydrogen energy yield.

CONCLUSIONS

The impact of reforming temperature and air activation rate on the gaseous reforming products composition and the reforming efficiency was studied using the plasma-catalytic reforming system based on rotating gliding discharge. The reforming efficiency obtained during the plasma-catalytic conversion of ethanol at approx. 250 °C is comparable to that of thermochemical conversion at > 700 °C or catalytic partial oxidation at approx. 500 °C. The highest reforming efficiency in the reforming temperature range of 200…350 °C was approx. 90 % at 250 °C. The flows of produced hydrogen, carbon monoxide and methane depend on the reforming temperature and during the experiment all had maxima at 250 °C. During the increase of the air activation rate the hydrogen production rate remains constant, while the carbon monoxide production rate decreases. This leads to the increase of H_2/CO ratio and to the decrease of reforming efficiency with the increase of air activation rate.

The energy yield of produced hydrogen decreases with the increase of air activation rate. The hydrogen energy yield of the plasma-catalytic reforming system with rotating gliding discharge reached 350 g/kWh. This value is among the highest values reached by the systems for the plasma-assisted conversion of ethanol.

ACKNOWLEDGEMENTS

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

REFERENCES

1. R.A. Sheldon, I. Arends, U. Hanefeld. *Green Chemistry and Catalysis*. Weinheim, Germany: "Wiley-VCH Verlag GmbH & Co". KGaA, 2007.
2. M. Crocker. *Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals*. Cambridge: "Royal Society of Chemistry", 2010.
3. S. Siddiqui, D. Friedman, J. Alper. *Opportunities and Obstacles in Large-Scale Biomass Utilization: The Role of the Chemical Sciences and Engineering Communities: A Workshop Summary*. The National Academies Press, 2012.
4. A. Fridman. *Plasma Chemistry*. Cambridge: Cambridge University Press, 2008.
5. O.A. Nedybaliuk, I.I. Fedirchyk, V.Ya. Chernyak, V. Bortyshevskyy, et al. Plasma-Catalytic Reforming of Raw Material for Biodiesel Production // *Plasma Physics and Technology*. 2015, v. 2, № 2, p. 171-174.
6. V.I. Parvulescu, M. Magureanu, P. Lukes. *Plasma Chemistry and Catalysis in Gases and Liquids*. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA, 2012.
7. L.V. Mattos, F.B. Noronha. Partial oxidation of ethanol on supported Pt catalysts // *Journal of Power Sources*. 2005, v. 145, № 1, p. 10-15.
8. R.L. Bain, L.L. Baxter, A.V. Bridgwater, K. Broer, et al. *Thermochemical Processing of Biomass*. Chichester, UK: John Wiley & Sons, Ltd, 2011.
9. C. Du, H. Li, L. Zhang, et al. Hydrogen production by steam-oxidative reforming of bio-ethanol assisted by Laval nozzle arc discharge // *International Journal of Hydrogen Energy*. 2012, v. 37, № 10, p. 8318-8329.
10. B. Sarmiento, J.J. Brey, I.G. Viera, et al. Hydrogen production by reforming of hydrocarbons and alcohols in a dielectric barrier discharge // *Journal of Power Sources*. 2007, v. 169, № 1, p. 140-143.
11. J. Henriques, N. Bundaleska, E. Tatarova, et al. Microwave plasma torches driven by surface wave applied for hydrogen production // *International Journal of Hydrogen Energy*. 2011, v. 36, № 1, p. 345-354.
12. D. Tsyganov, N. Bundaleska, E. Tatarova, C.M. Ferreira. Ethanol reforming into hydrogen-rich gas applying microwave ‘tornado’-type plasma // *International Journal of Hydrogen Energy*. 2013, v. 38, № 34, p. 14512-14530.
13. E. Tatarova, N. Bundaleska, F. Dias, et al. Hydrogen production from alcohol reforming in a microwave ‘tornado’-type plasma // *Plasma Sources Science and Technology*. 2013, v. 22, p. 65001.
14. B. Hrycak, D. Czylkowski, R. Miotk, M. Dors, M. Jasinski, J. Mizeraczyk. Hydrogen production from ethanol in nitrogen microwave plasma at atmospheric pressure // *Open Chemistry*. 2014, v. 13, p. 317-324.
15. G. Petitpas, J. Gonzalez-Aguilar, A. Darmon, L. Fulcheri. Ethanol and E85 Reforming Assisted by a Non-thermal Arc Discharge // *Energy & Fuels*. 2010, v. 24, № 4, p. 2607-2613.
16. G. Petitpas, J. Rollier, A. Darmon, et al. A comparative study of non-thermal plasma assisted reforming technologies // *International Journal of Hydrogen Energy*. 2007, v. 32, № 14, p. 2848-2867.
17. K. Hadidi, L. Bromberg, D. Cohn, A. Rabinovich, et al. Hydrogen-Rich Gas Production from Plasmatron Reforming of Biofuels // *World Renewable Energy Congress VIII and Expo*, 2004, PSFC/JA-04-22, p. 5.

Article received 23.10.2016

ПЛАЗМЕННО-КАТАЛИТИЧЕСКОЕ РЕФОРМИРОВАНИЕ ЭТАНОЛА: ВЛИЯНИЕ СТЕПЕНИ АКТИВАЦИИ ВОЗДУХА И ТЕМПЕРАТУРЫ РЕФОРМИРОВАНИЯ

О.А. Недыбалюк, В.Я. Черняк, И.И. Федирчик, В.П. Демчина, В.А. Бортышевский, Р.В. Корж

Изложено исследование влияния степени активации воздуха и температуры реформирования на состав газообразных продуктов плазменно-каталитического реформирования этанола и на его эффективность. Анализ состава полученных продуктов показал, что эффективность реформирования имеет максимум в исследованном диапазоне температур. Исследованная система имеет высокую эффективность реформирования и высокий энергетический выход водорода при температурах ниже, чем в традиционных технологиях реформирования.

ПЛАЗМОВО-КАТАЛІТИЧНЕ РЕФОРМУВАННЯ ЕТАНОЛУ: ВПЛИВ СТУПЕНЮ АКТИВАЦІЇ ПОВІТРЯ ТА ТЕМПЕРАТУРИ РЕФОРМУВАННЯ

О.А. Недибалюк, В.Я. Черняк, І.І. Федірчик, В.П. Демчина, В.А. Бортишевський, Р.В. Корж

Представлено дослідження впливу ступеня активації повітря та температури реформування на склад газоподібних продуктів реформування етанолу та на його ефективність. Аналіз складу продуктів реформування показав, що ефективність реформування має максимум у дослідженому діапазоні температур реформування. Досліджена система забезпечує високу ефективність реформування та високий енергетичний вихід водню за температур, що є нижчими, ніж у традиційних технологіях реформування.