

HYBRID PLASMA-CATALYTIC REFORMING OF ETHANOL AEROSOL

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Hybrid plasma-catalytic reforming of the ethanol aerosol with plasma activation of only the oxidant (air) was studied. Part of the oxidant (~20%) was activated by means of rotational gliding arc with solid electrodes and injected into the reaction (pyrolytic) chamber as a plasma torch. This part of the oxidant interacted with a mixture of hydrocarbons and the rest of the oxidant (~80%) in the reaction chamber. Temperature changes in the reaction chamber, the composition of the synthesis-gas and the products of synthesis-gas combustion were analyzed.

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INTRODUCTION

Some of the already conducted research clearly established that using plasma for direct conversion of hydrocarbons is less economically viable [1] when comparing with plasma catalysis. Plasma as a source of active particles can activate and significantly accelerate the plasma-chemical conversion. The injected plasma can be generated by low power discharge.

Plasma-liquid system (PLS), which is based on low-powered rotating gliding arc with solid electrodes, was used in researches of reforming process of hydrocarbons. The process of hydrocarbons partial oxidation was used as a main reaction for reforming. During plasma-catalytic reforming process only an oxidant is activated by a discharge and then mixed with a hydrocarbon [2, 3]. The plasma reforming has one essential difference – oxidant and hydrocarbon are simultaneously processed by the discharge [4].

1. EXPERIMENTAL SETUP

Fig. 1 shows the scheme and photo of the hybrid plasma-liquid system with low power rotational gliding arc with solid electrodes purposed for plasma-catalysis reforming of ethanol aerosol. System uses the prototype discharge chamber from the PLS with reverse vortex gas flow type tornado with liquid electrode [5, 6], but without liquid and with much shorter distance between the solid electrodes. System consists of cylindrical plasma chamber made of glass and sealed on both ends with metal flanges. Its diameter is 90 mm and height is 32 mm. T-like electrode (with a 30 mm diameter) is placed through a hole in bottom flange and upper flange has a hole with stainless steel sleeve in it, which works as a second electrode. Both electrodes are water-cooled through cooling channels. The distance between the electrodes is 1 mm. Power was supplied by a DC power source, which provided voltage up to 7 kV.

Upper flange has an inlet for oxidant, which directs its flow into circular channel in such way that to form a

vortex. The oxidant moves through discharge leading to plasma generation. Through this way, about 20% of total amount of oxidant are introduced into the system. The hole in upper flange allows plasma to get into pyrolytic chamber. In its upper part, pyrolytic chamber has an inlet for aerosol of hydrocarbon mixed with the rest 80% of oxidant.

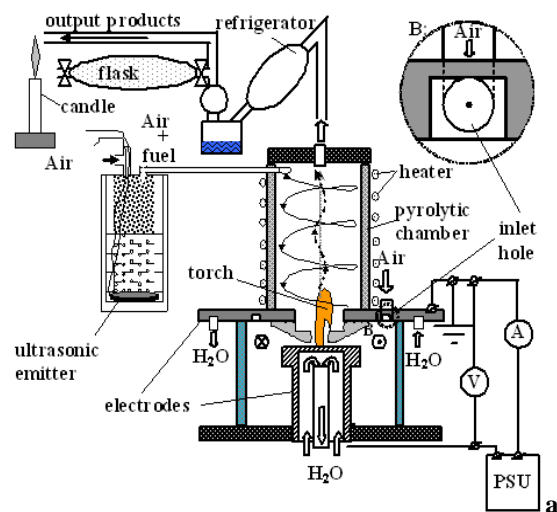


Fig. 1. Scheme (a) and photo (b) of PLS for hybrid plasma-catalytic reforming of ethanol aerosol

Fuel inlet is set to create a reverse vortex flow of fuel, as it descends along inner chamber wall towards plasma. Reforming products rise to the top exit from the chamber along its axis by employing so-called “tornado” effect. Pyrolytic/reaction chamber has cylindrical shape with an inner diameter of 42 mm, outside diameter 46 mm and height of 100 mm, and is made of stainless steel. With the help of heating element the temperature of pyrolytic chamber could be maintained in the range of 100...900 °C. The external wall of the pyrolytic chamber has two thermocouples attached at heights of 15 mm (T-down) and 75 mm (T-upper) to determine the temperature of the outer wall of pyrolytic chamber from below and from above, respectively.

Hydrocarbon was fed into the reaction chamber as an aerosol. Aerosol was formed by ultrasound emitter with a frequency of ~ 800 Hz. Mixture of hydrocarbon aerosol with 80% of total oxidant was fed tangentially through the channel to the lateral wall of the reaction (pyrolytic) chamber, forming reverse vortex flow of “tornado” type. Because this system could work for a long time, it was decided to avoid the accumulation of synthesis-gas by burning the output products of the reforming.

Combination of pyrolysis and plasma catalysis is what makes this a hybrid system. Separate injection of plasma and fuel reduces hydrocarbon impact on plasma and keeps plasma non-isothermal. The system has a refrigerator before its exit, which decreases the temperature of exhaust gases to the room level. Part of conversion products is condensed and kept as a sample after cooling, part is stored in a flask as gas and a candle burns the rest of them to prevent an accumulation of high-flammable gases in a laboratory.

Ethanol (96% ethyl alcohol) was chosen as model hydrocarbon. The air was used as a working gas (oxidizing agent). The airflow ($33 \text{ cm}^3 \cdot \text{s}^{-1}$) was injected into reaction chamber with rotational gliding arc discharge, providing plasma activation of an oxidant. The reaction chamber was fed a mixture of air ($142 \text{ cm}^3 \cdot \text{s}^{-1}$) with ethanol aerosol ($0.17 \text{ ml} \cdot \text{s}^{-1}$).

At the beginning of experiments pyrolytic chamber was always heated to a temperature of 485 °C, system had continuous air supply in $33 + 142 \text{ cm}^3 \cdot \text{s}^{-1}$ range. Ignited discharge had a current set at 100 mA, while the discharge voltage was in range of 600...750 V. Then high-frequency ultrasonic transducer was turned on to supply the system with ethanol aerosol. Several modes of ethanol reforming were investigated: when the temperature of the external heater of the reaction chamber did not change during the work; when at the beginning the voltage, which powered external heating, was reduced by 10, 15 and 25%.

The efficiency of the reforming system is characterized by the coefficient of transformation of electrical energy into the heat of complete combustion of produced synthesis-gas – α [7]. A following formula is used to calculate α :

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

where Syngas_i – components of synthesis-gas, $\text{LHV}(\text{Syngas}_i)$ – calorific value of i -th component of synthesis-gas, IPE – energy invested in the discharge.

2. RESULTS AND DISCUSSION

The influence of plasma on the process of ethanol reforming was investigated by studying the mode with turned off discharge and turned on external heating of pyrolytic chamber. In this case, the initial temperatures of the outer wall of the pyrolytic chamber $T_{\text{down}} = T_{\text{upper}} = 485 \text{ °C}$ and slightly decreased during experiment. Output gas, in this case, consisted of 77.24% – N_2 , 19.33% – O_2 , 2.71% – H_2O , 0.06% – CO_2 , 0.66% – $\text{C}_2\text{H}_5\text{OH}$. Since there was no synthesis-gas (H_2 and CO) and other light hydrocarbons (CH_4 , C_2H_4 , C_2H_2 , C_2H_6) in the output gas the coefficient of electrical energy transformation $\alpha = 0$. In the system without plasma reforming processes did not occur.

The distribution of the outer wall temperature of pyrolytic chamber during plasma catalytic reforming of ethanol aerosol in dependence on the duration of system work and after it is turned off was analyzed. In case of discharge absence, the temperature slightly decreased. Temperature inside the chamber slowly increased during experiments with plasma activation of oxidant, except for the case of external heating voltage reduction at 25 %, where it remained constant. Special attention should be paid to processes that occur after discharge turns off and ethanol aerosol stops to be fed into the system (Fig. 2).

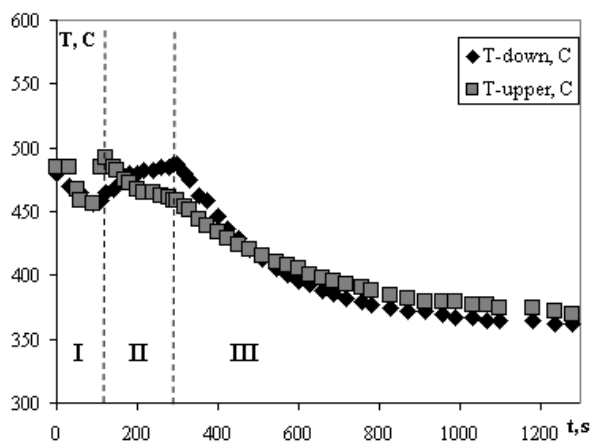


Fig. 2. Temperature distributions in the reaction chamber during the system running (I), after switching off the plasma torch (II) and cessation of ethanol in the system (III), for the case when external heating voltage was reduced by 25% after the start of the system work

It should be noted that after rotating gliding arc was turned off there were sharp and rapid changes of pressure inside the system, which lasted about 30 seconds, after which the initial gas flow rate was reduced to $\sim 200 \text{ cm}^3 \cdot \text{s}^{-1}$, at the same time the working gas supply system was stable ($175 \text{ cm}^3 \cdot \text{s}^{-1}$). Although high-frequency ultrasonic transducer was turned off, the airflow seized previously formed droplets and vapors of ethanol. This may explain the higher value of the gas flow at the outlet of the system in comparison to the entrance. The value of the gas flow at the system output was equal to what was fed into the system ($175 \text{ cm}^3 \cdot \text{s}^{-1}$).

after a few minutes of work. Ethanol vapor still got into the reaction chamber carried by air, but the temperature was too small for ethanol pyrolysis to occur.

Relative concentrations of the gas components at the outlet of the system for different modes of conversion is shown in Table 1. The coefficient of electrical energy transformation α for studied modes was calculated according to the results of gas chromatography. They are given in the last row of Table 1.

Table 1. Relative concentrations of gas components at the outlet of the system while the voltage of the external heater was reduced by 10, 15, and 25% after turning on the discharge

Substance	T=565 °C	T=560 °C	T=485 °C
H ₂	12.03	13.26	13.05
CO	17.86	18.28	17.28
CH ₄	6.68	9.91	11.63
C ₂ H ₄	1.47	2.99	4.88
C ₂ H ₂	0.53	0.62	0.46
C ₂ H ₆	0.17	0.3	0.94
C ₃ H ₈	0	0	0.07
iC ₄ H ₁₀	0.11	0	1.05
O ₂	0	0	0
N ₂	53.1	47.85	43.09
CO ₂	3.5	2.99	2.03
C ₂ H ₅ OH	0.74	0.63	2.45
H ₂ O	3.1	3.17	3.07
α	38	42	56

Studies have shown the absence of oxygen in the produced gas, which may indicate that all of it was used for the conversion and combustion. Relative concentration of nitrogen is reduced by increasing the gas flow at the outlet of the system while keeping the flow of air at the inlet stable (175 cm³·s⁻¹). Lowering the temperature of the external heater slightly affects the content of H₂ and CO, but increases the percentage of methane (CH₄), ethylene (C₂H₄) and ethane (C₂H₆). It should be noted that in the studied system H₂ concentration is lower than the CO concentration.

Coefficient of electrical energy transformation is higher due to increased percentage of CH₄, C₂H₄ and C₂H₆ in the output gas and decreased temperature of external heating of pyrolytic chamber. It is also worth noting that the value of α was by an order of magnitude higher during plasma catalytic reforming when compared with plasma reforming of ethanol. The obtained results allow for a comparison of the gas components and coefficient α between the systems

Table 2. Results of conversion of various hydrocarbons into synthesis-gas using plasma and plasma-catalytic reforming

Method	Reference	Hydrocarbons	H ₂	CO	CH ₄	C ₂ H ₄	C ₂ H ₂	H ₂ /CO	α
Plasma reforming	[8-10]	Bioethanol	26	14	0.9	0.5	0.5	1.77	0.8
	[11-12]	Bioethanol (CO ₂ -17%)	31	23	4	0.4	0.9	1.36	1.5
	[4]	C ₂ H ₅ OH	36	23	1.2		0.8	1.57	1.8
Plasma-catalytic reforming	[2]	C ₂ H ₅ OH	19...28	9...22	0...6.1	0...1.1	0	1.1...3	18...44
	[3]	C ₂ H ₅ OH	55	12	10	1		4.58	15.8
	-	C ₂ H ₅ OH	12...13	18	7...12	1.5...5	0.5...0.6	0.6...0.8	38...56

studied in this work and those presented in other sources. This comparison is depicted in Table 2.

It is clear from the results presented in the table that the use of plasma catalysis for hydrocarbon conversion by an order of magnitude increases the coefficient of electrical energy transformation and allows for effective reforming of the gaseous and liquid fuels of varying viscosity with smaller input of electrical energy. The output synthesis-gas was burnt to avoid the accumulation of large quantities of exhaust gas (Fig. 3).

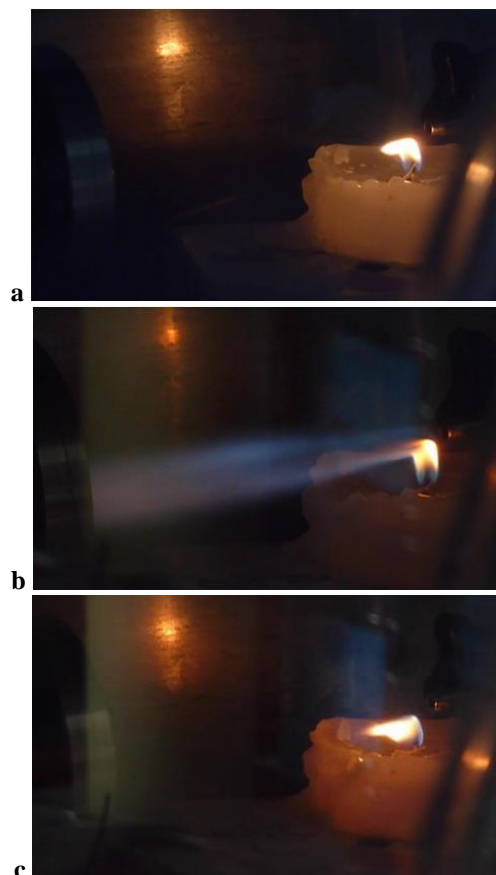


Fig. 3. Photos of output gas burning during different modes of the system: a – discharge is “off”, heater is “off”; b – discharge is “on”, heater is “on”; c – discharge is “off”, heater is “on”

Research of the flame of burned output gas showed that the flame at the system output disappeared after rotational gliding arc discharge was switched off, which implies that ethanol conversion into synthesis-gas in system only occurs through plasma activation process. The flame intensity varied depending on the speed of the output gas. The flame reached 5 cm in diameter at a distance of ~ 10 cm, its length exceeded 50 cm.

CONCLUSIONS

When the temperature of reaction chamber is ≤ 600 °C, ethanol conversion into synthesis-gas occurs only in presence of plasma activation processes. Therefore, it is possible to use plasma for effective management of the reforming process.

Coefficient of the electrical energy transformation is by an order of magnitude higher in a case of hybrid plasma-catalytic conversion of ethanol in comparison with plasma conversion. This leads to more efficient reforming with less electrical energy spent.

Temperature in pyrolytic reactor is considerably lower during hybrid plasma-catalytic conversion of ethanol aerosol than during conventional pyrolysis.

REFERENCES

1. A. Czernichowski. Conversion of waste glycerol into synthesis gas // *19th International Symposium on Plasma Chemistry (ISPC-19), Bochum, Germany, July 26-31, 2009*. 2009.
2. A. Czernichowski, K. Wesolowska. Generation of the sintesis gas from bioethanol // *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* 2006, v. 51, № 2.
3. L. Bromberg, D.R. Cohn, K. Hadidi, J. Heywood, A. Rabinovich. Diesel engine emission reduction (DEER) // *Workshop, Coronado, CA*. 2004.
4. V.I. Arkhipenko, S.M. Zgirouski, A.G. Karoza, A.A. Kirillov, L.V. Simonchik. Diagnostics of ethanol conversion products by IR absorption spectroscopy // *Journ Appl. Spectroscopy*. 2013, v. 80, № 1, p. 99-103.
5. O.A. Nedybaliuk, V.Y. Chernyak, S.V. Olszewski. Plasma-liquid system with reverse vortex flow of "tornado" type (TORNADO-LE) // *Problems of Atomic Science and Technology (16)*. 2010, N6, p. 135-137.
6. O.A. Nedybaliuk, V. Ya. Chernyak, S.V. Olszewski, E.V. Martysh. Dynamic plasma-liquid system with discharge in reverse vortex flow of "tornado" type // *International Journal of Plasma Environmental Science & Technology*. 2011, v. 5, № 1, p. 20-24.
7. V.Ya. Chernyak, S.V. Olszewski, V.V. Yukhymenko, et al. Plasma-assisted reforming of ethanol in dynamic plasma-liquid system: Experiments and Modeling // *IEEE Transactions on plasma science*. 2008, v. 36, № 6, p. 2933-2939.
8. D.S. Levko, A.I. Shchedrin, V.Y. Chernyak, S.V. Ol'shevskii, O.A. Nedybalyuk. 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.
9. V.Ya. Chernyak, O.A. Nedybaliuk, V.V. Yukhymenko, et al. Reforming of simple hydrocarbons in plasma liquid systems // *19th Symposium on Physics of Switching Arc, FSO 2011, 5-9 September 2011, Brno, Czech Republic*. 2011, p. 17-26.
10. V. Chernyak, O. Nedybaliuk, E. Martysh, S. Olszewski, O. Solomenko, A. Shchedrin, D. Levko, V. Demchina, V. Kudryavzev. Plasma reforming of liquid hydrocarbon in plasma-liquid systems // *Nukleonika*. 2012, v. 57, № 2, p. 301-305.
11. O.A. Nedybaliuk, O.I.V. Solomenko, V.Ya. Chernyak, E.V. Martysh, T.E. Lisitchenko, L.V. Simonchik, V.I. Arkhipenko, A.A. Kirillov, A.I. Liptuga, N.V. Belenok. 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.
12. A.N. Tsybalyuk, D.S. Levko, V.Y. Chernyak, E.V. Martysh, O.A. Nedybalyuk, E.V. Solomenko. 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.

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ГИБРИДНОЕ ПЛАЗМЕННО-КАТАЛИТИЧЕСКОЕ РЕФОРМИРОВАНИЕ АЭРОЗОЛЯ ЭТАНОЛА

Е.В. Соломенко, О.А. Недыбалиук, В.Я. Черняк, В.В. Юхимеко, Ю.П. Веремий, К.В. Юхимнко, Е.В. Мартыш, В.П. Демчина, И.И. Федирчик, Д.С. Левко, О.Н. Цимбалиук, А.И. Липтуга, С.В. Драгнев

Исследовано гибридное плазменно-каталитическое реформирование аэрозоля этанола с плазменной активацией исключительно окислителя (воздуха). Часть окислителя (~20%) активировалась с помощью вращательной скользящей дуги с твердыми электродами и вводилась в виде плазменного факела в реакционную (пиролитическую) камеру. Эта часть окислителя взаимодействовала со смесью углеводорода и остальной частью окислителя (~80%) в реакционной камере. Были проанализированы изменения температуры реакционной камеры, состав синтез-газа и продуктов пламени синтез-газа.

ГІБРИДНЕ ПЛАЗМОВО-КАТАЛІТИЧНЕ РЕФОРМУВАННЯ АЕРОЗОЛЮ ЕТАНОЛУ

О.В. Соломенко, О.А. Недыбалиук, В.Я. Черняк, В.В. Юхимеко, Ю.П. Веремий, К.В. Юхимнко, Є.В. Мартыш, В.П. Демчина, І.І. Федірчик, Д.С. Левко, О.М. Цимбалиук, А.І. Липтуга, С.В. Драгнев

Досліджено гібридне плазмово-каталітичне реформування аерозолі етанолу з плазмовою активацією виключно окисника (повітря). Частина окисника (~20%) активувалась за допомогою обертальної ковзної дуги з твердими електродами і вводилась у вигляді плазмового факела в реакційну (піролітичну) камеру. Ця частина окисника взаємодіяла з сумішшю вуглеводню та іншою частиною окисника (~80%) в реакційній камері. Зміни температури реакційної камери, склад синтез-газу та продуктів полум'я синтез-газу були проаналізовані.