Plasma-Catalytic Reforming of Raw Material for Biodiesel Production

Nedybaliuk O.[1], Fedirchyk I.[1], Chernyak V.[1], Bortyshevskyy V.[2],
Iukhymenko V.[1], Korzh R.[2], Demchina V.[3], Dragnev S.[4]

[1] Taras Shevchenko National University of Kyiv, 64/13, Volodymyrska Street, City of Kyiv, 01601, Ukraine, e-mail: oanedybaliuk@gmail.com
[2] Institute of Bioorganic Chemistry and Petrochemistry of NASU, 50, Kharkivske Shosse, City of Kyiv, Ukraine
[3] Gas Institute of NASU, 39 Degtyarivska Street, City of Kyiv, 03113, Ukraine
[4] National University of Bioresources and Environmental Sciences of Ukraine, 15, Heroyiv Oborony Street, City of Kyiv, 03041, Ukraine

Plasma-catalytic reforming of liquid hydrocarbons is considered in this paper. Rotating gliding discharge was used as the generator of non-equilibrium plasma. Vegetable oil (raw materials for the production of bio-diesel) and ethanol were used as model hydrocarbons. Efficiencies and transformation coefficients for the processes of vegetable oil and ethanol reforming are calculated.

Keywords: plasma-catalytic reforming, rotating gliding discharge, synthesis gas, ethanol, vegetable oil

1   INTRODUCTION

Today the debates among specialists on a limited amount of fossil hydrocarbons are still going. However, it is unarguable that the burning of fossil hydrocarbons leads to heavy CO_2 emission into the atmosphere, which enhances the greenhouse effect. Therefore, there is an interest in renewable biofuels, which are made from plants or biomass. CO_2 is released during biofuel combustion, but it is absorbed from the atmosphere by plants during their growth. Bioethanol and biodiesel can be viewed as the examples of such biofuels. However, during biodiesel production nearly $10 \div 20$ % of all products are waste, the main component of which is bioglycerol [1]. The large-scale production of biodiesel raises the question about the usage and utilization of bioglycerol as the main waste. Therefore, it is promising to directly reform the raw material from which biodiesel is produced into synthesis gas and then burn this synthesis gas to generate the heat or to synthesize the synthetic fuels (dimethyl ether). Through this method, it is possible to avoid the problems with waste creation and utilization of bioglycerol.

The usage of dynamic plasma systems for the conversion of liquid hydrocarbons into synthesis gas is among the most promising directions in modern plasma chemistry. The dynamic plasma systems with a vortex [2–4] and reverse vortex [5,6] gas flow have additional factors that strongly affect the energy parameters of plasma, in contrast to the classic gas discharges. As a source of active species, plasma can initiate and significantly accelerate plasma-chemical conversion reactions. The plasma reforming [6–8] of hydrocarbons is not economically efficient [6] in comparison to plasma-catalytic reforming [6,9–14], where plasma is used only as a catalyst. Plasma catalysis can increase the efficiency of reforming of hydrocarbons into synthesis gas [15]. In addition, it is important to create conditions aimed at the generation of exactly nonequilibrium plasma, which will increase conversion selectivity. The use of plasma-catalytic reforming, with only oxidant being activated by a discharge, will provide both high efficiency and nonequilibrium plasma [14,15].

2   EXPERIMENTAL SET-UP

To study the process of plasma-catalytic biofuels reforming, the dynamic plasma system (Fig.1) with rotating gliding discharge and solid electrodes was used. This system does not feature a water cooling. The reforming system consists of a cylindrical discharge chamber (1) and a reaction (pyrolytic) chamber (2). Both chambers are made of stainless steel. A conical electrode (3) was introduced into the chamber through a dielectric sleeve (4) in the metal flange. This electrode was used as an anode and was under high potential. The discharge was burning between the conical T-shaped electrode (3) and the stainless steel sleeve (5), which was used as a cathode and was grounded. Discharge glides on the surface

of both electrodes. The interelectrode distance is 1 mm. An oxidant flow was injected through a channel (6), tangent to a sidewall of the discharge chamber (1), forming a vortex flow (7). A plasma torch was injected into the reaction chamber (2). A mixture of the hydrocarbons and water steam was introduced through a hole (8) and oxidant was introduced through hole (9), both of them tangentially to the sidewall of reaction chamber (2), forming a "tornado" reverse vortex flow (10). Rotating mixture of hydrocarbons, water vapor and oxidant goes up (11) to the top of reaction chamber, moves to the central chamber axis, where plasma-activated oxidant (12) is injected into reaction chamber, and then moves down. The synthesis gas (13) exits pyrolytic chamber through a hole (14). Due to the fact that the system can work continuously for a long time, produced synthesis gas was burned in calorimeter to avoid its accumulation and ensure its safe disposal.
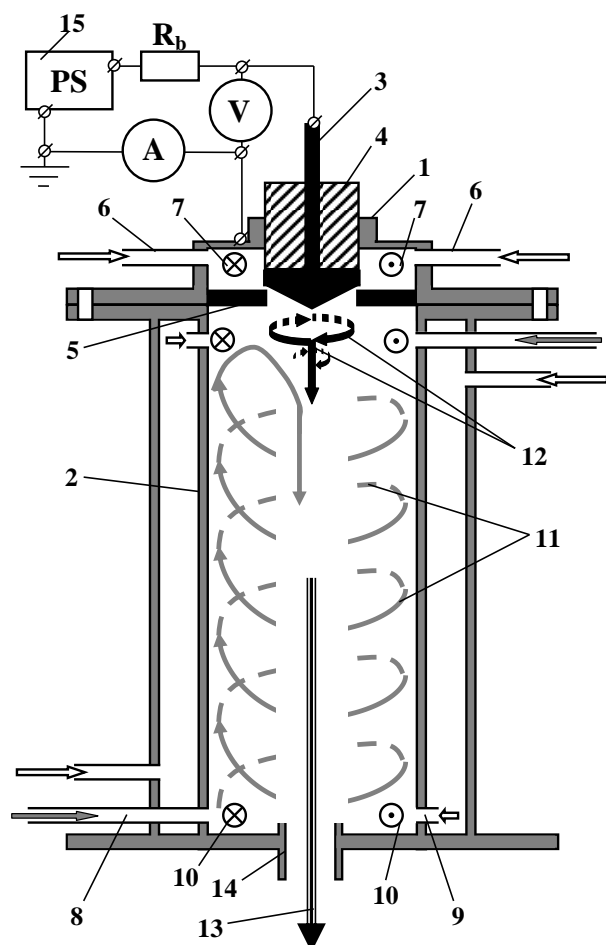

Fig.1: Schematic representation of dynamic plasma system with rotating gliding discharge and solid electrodes

Produced gas can be burned by a transverse arc, or in a standard hot water boiler, which is designed to work on natural or liquefied gas.

The DC power supply (15) has an open circuit voltage of 7 kV. With the ballast resistance (R_b) of $4 \div 30$ kOhm, the current of stable discharge was $50 \div 250$ mA. During plasma-catalytic reforming of hydrocarbons, the highest maintained wall temperature of pyrolytic chamber was 450 °C.

The vegetable oil and ethanol were used as model hydrocarbons. The main component of vegetable oil is oleic acid ($C_{17}H_{33}COOH$). Room temperature air was used as a model oxidant. Below is the example of partial oxidation reaction of ethanol (C_2H_5OH):

$$C_2H_5OH + 1/2 O_2 \rightarrow 2CO + 3H_2, \qquad (1)$$
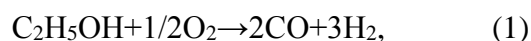
With the presence of H_2O the water-gas shift reaction is possible:

$$CO + H_2O \rightarrow CO_2 + H_2. \qquad (2)$$
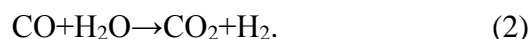
During research, the gas chromatography and mass-spectrometry analysis of synthesis gas samples, which were collected into tubes, were conducted using Agilent 6890N chromatograph and MX–7301 monopole mass-spectrometer [8].

3 RESULTS AND DISCUSSION

The discharge current-voltage characteristics are shown at Fig. 2. They were measured at different air flows into discharge chamber. The discharge current-voltage characteristics are similar to the current-voltage characteristic of an electric arc.
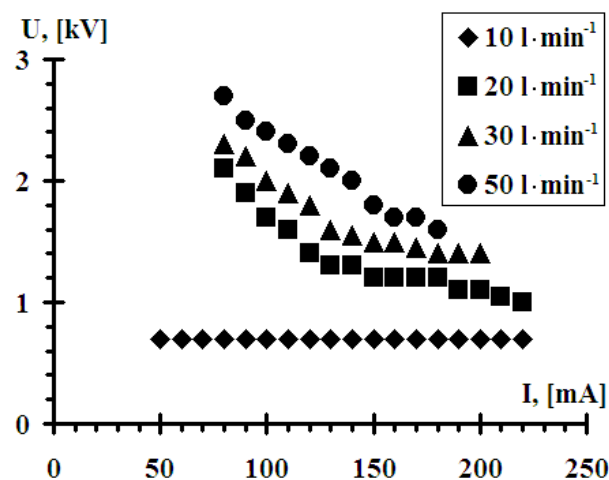

Fig.2: Current-voltage characteristics of the rotating gliding discharge

Air and hydrocarbon flows were chosen in order to match the stoichiometry of the partial oxidation reaction. It should be noted that the flow of air in the case of vegetable oil is 2 times higher in comparison with ethanol. Table 1 presents the composition of synthesis gas formed during plasma-catalytic reforming of vegetable oil and ethanol, which was obtained using gas chromatography. Because nitrogen does not react and only appears as a ballast gas, results are normalized to the value of the volume concentration of N_2. CO was not observed for vegetable oil; this indicates that all produced CO takes part in the reaction (2). Hydrogen concentration in synthesis gas obtained from ethanol is almost 1.5 times higher in comparison with synthesis gas obtained from vegetable oil. However, it should be noted that the flow of synthesis gas in the case of vegetable oil is 2 times greater.

Fig.3 shows the mass-spectra of reforming products for both ethanol and vegetable oil conversion obtained by MX–7301 monopole mass-spectrometer from same samples used for gas chromatography. Mass-spectra are in agreement with gas chromatography results. Additionally, theoretically possible yield of methanol (CH_3OH) and dimethyl ether (C_2H_6O) from syngas, formed during plasma-catalytic reforming of ethanol and vegetable oil, was calculated. The yield of methanol and dimethyl ether in case of vegetable oil is 1.4 times higher in comparison with ethanol. Therefore, from an economic point of view vegetable oil is more favorable feedstock for dimethyl ether production. The efficiency η of reforming could be calculated from the lower heating value (LHV) of products and reactants, which is the heat available when using a fuel without taking into account the condensation of formed water, as follows [16,17]:

$$\eta = \frac{(LHV\ of\ products) \times 100\ \%}{Plasma\ power + LHV\ of\ reactants},\ (3)$$

where *LHV of products* is the lower heating value of reforming products, *Plasma power* is the electrical energy needed to generate plasma, calculated from current-voltage characteristics, *LHV of reactants* − the lower heating value of reactants. The LHVs in (3) can be substituted with the power values.

Table.1: Main components of synthesis gas formed during plasma-catalytic reforming of vegetable oil (N_2 volume fraction is 10 %) and ethanol (N_2 volume fraction is 11.6 %)

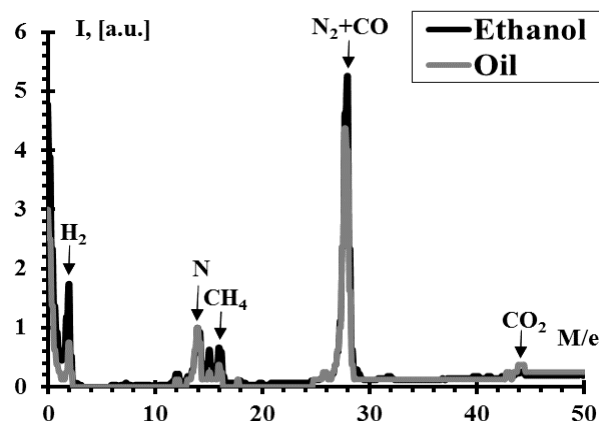|	H_2, [a.u.]	CO, [a.u.]	N_2, [a.u.]
Vegetable oil	0.34	0.00	1.00
Ethanol	0.51	0.06	1.00

Fig.3: Mass-spectra of ethanol and vegetable oil reforming products; all components are normalized on N (M/e = 14) peak intensity

The electrical energy transformation coefficient (α) of reforming system is calculated via following formula:

$$\alpha = \frac{LHV\ of\ products}{Plasma\ power},\ (4)$$

A research was conducted to determine the dependence of η and α from the flow of water vapor. During this study, the input flow of ethanol was set to be equivalent to 15 kW. Discharge power was 130 W. Fig.4 shows the dependence of α and η during plasma-catalytic reforming of ethanol on $C_2H_5OH : H_2O$ ratio. It is evident from the measured values of η and α, that they both have maxima at $C_2H_5OH : H_2O = 1.7:1.0$. The optimal operation mode for researched system during plasma-catalytic reforming of ethanol lies in an area where reforming efficiency η equals 85 % and electrical energy transformation coefficient α is approximately 100. Obtained ratio was used for the vegetable oil reforming. Further calculations showed that reforming efficiency of the system during plasma-catalytic reforming of oil was 87 %, which is substantially higher in comparison to approximately 70 % obtained in other similar research [18]. α

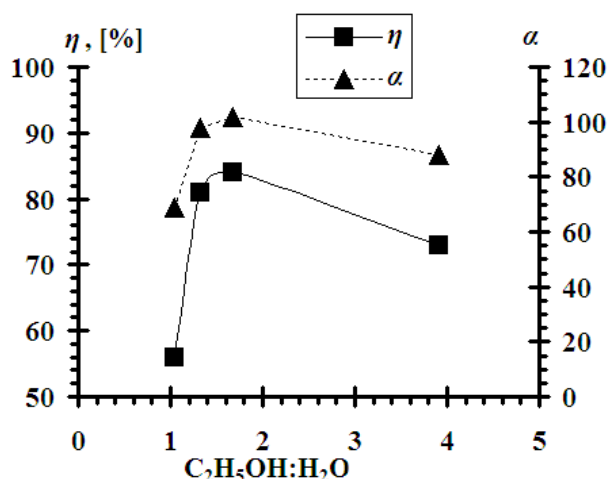obtained in case of oil reforming was 98.

Fig.4: Dependence of reforming efficiency η and electrical energy transformation coefficient α on $C_2H_5OH:H_2O$ ratio during plasma-catalytic reforming of ethanol

Calorific values of reforming products per one kilogram of feedstock are 25 MJ/kg for ethanol and 33 MJ/kg for vegetable oil, which makes oil a more appealing reforming feedstock from the economic standpoint.

4   CONCLUSION

The study of plasma-catalytic reforming of biofuels has shown that plasma-catalytic reforming of vegetable oil and ethanol shows the electric energy transformation coefficient of $\alpha \approx 100$, and the reforming efficiency of $\eta \approx 85\,\%$. From the economic point of view, vegetable oil, which is the raw material for biodiesel production, is better feedstock for the production of synthesis gas and for synthesis of dimethyl ether in comparison to ethanol.

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