# Plasma-Catalytic Reforming of Bio-Fuels and Diesel Fuel

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*Abstract*—The replacement of fossil hydrocarbons with the renewable biomass alternatives is an inevitable requirement in our transition towards a sustainable economy. However, traditional petrochemical technologies are not designed to operate using biomass raw materials. Thus, the development of new hydrocarbon processing methods is essential. This paper deals with the study of the hybrid plasma-catalytic reforming of liquid hydrocarbons. The system for the reforming of liquid hydrocarbons, which used low-power rotating gliding discharge as a plasma generator, was studied. Sunflower oil ($C_{17}H_{33}COOH$) and ethanol ($C_2H_5OH$) have been used as model oxygen-containing hydrocarbons and diesel fuel ($C_{16}H_{34}$) has been used as a model hydrocarbon without oxygen. Reforming products have been analyzed using mass spectrometry and gas chromatography, the combustion of produced syngas was studied. The values of the reforming efficiency, the ratio between the chemical energy of the produced syngas and the electric energy spent on the plasma generation, and the efficiency of the produced syngas combustion in the standard water heaters, were obtained.

*Index Terms*—Atmospheric-pressure plasmas, biomass, plasma-catalytic reforming, plasma chemistry, rotating gliding discharge.

## I. INTRODUCTION

IT is common knowledge that the combustion of fossil hydrocarbons enhances the greenhouse effect due to the emission of $CO_2$ into the atmosphere. In addition, the extraction of fossil hydrocarbons is accompanied by methane emission, which has 20 times higher Global Warming Potential than $CO_2$ [1]. Therefore, there is a growing interest in renewable hydrocarbon bio-fuels produced from plants or biomass. Bio-fuels still release $CO_2$ during combustion, but plants absorb it during their growth, creating a biomass-to-bio-fuel $CO_2$ cycle. Ethanol and bio-diesel are the most common examples of such bio-fuels.

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However, near 20 % of the products formed during the bio-diesel production is a waste, with bio-glycerin as its main component. Bio-glycerin combustion causes the formation of harmful substances, such as acrolein [2]. The large-scale production of bio-diesel raises the problem of utilization and disposal of bio-glycerin. Thus, the new approach has been suggested to solve this problem – the direct reforming of the renewable raw material into syngas. Syngas can be burned to generate heat or used in the production of synthetic fuels, such as dimethyl ether (DME), and valuable organic chemical compounds, such as detergents, adhesives or pesticides. Such approach makes it possible to avoid the problems connected with the production and disposal of bio-diesel production waste. Thermochemical and catalytic conversion methods for the production of syngas from the renewable hydrocarbons are intensely studied in countries with the access to a large amount of waste biomass [3]–[6].

The use of dynamic plasma systems for the conversion of hydrocarbon raw materials into syngas is one of the most promising directions in modern plasma chemistry [7]–[11]. Dynamic plasma systems with vortex [12]–[14] and reverse vortex [15], [16] gas flows have additional factors that strongly affect the energy parameters of plasma in contrast to classical gas discharges. As a source of active particles, plasma can initiate and significantly accelerate plasma-chemical conversion reactions. The plasma reforming of hydrocarbons [16]–[19] is not economically efficient [16] compared to hybrid plasma-catalytic reforming [7], [16], [20]–[24], where plasma is used only as a catalyst [16], [25], [26]. Plasma catalysis can increase the hydrocarbons reforming efficiency into syngas [27]. In addition, it is important to create conditions for the generation of the non-equilibrium plasma to increase the reforming selectivity. The use of hybrid plasma-catalytic reforming, during which only the oxidant is activated by the discharge, provides both high energy efficiency and non-equilibrium plasma generation [25], [27].

The main goal of this work is to determine the effectiveness of reforming renewable and heavy fossil hydrocarbons using plasma-catalytic reforming system. Additionally, we aim to determine the possibility of using the gaseous reforming products in the standard heating devices.

## II. EXPERIMENTAL SETUP

A three-component experimental setup was used to study the hybrid plasma-catalytic reforming of bio-fuels. The setup
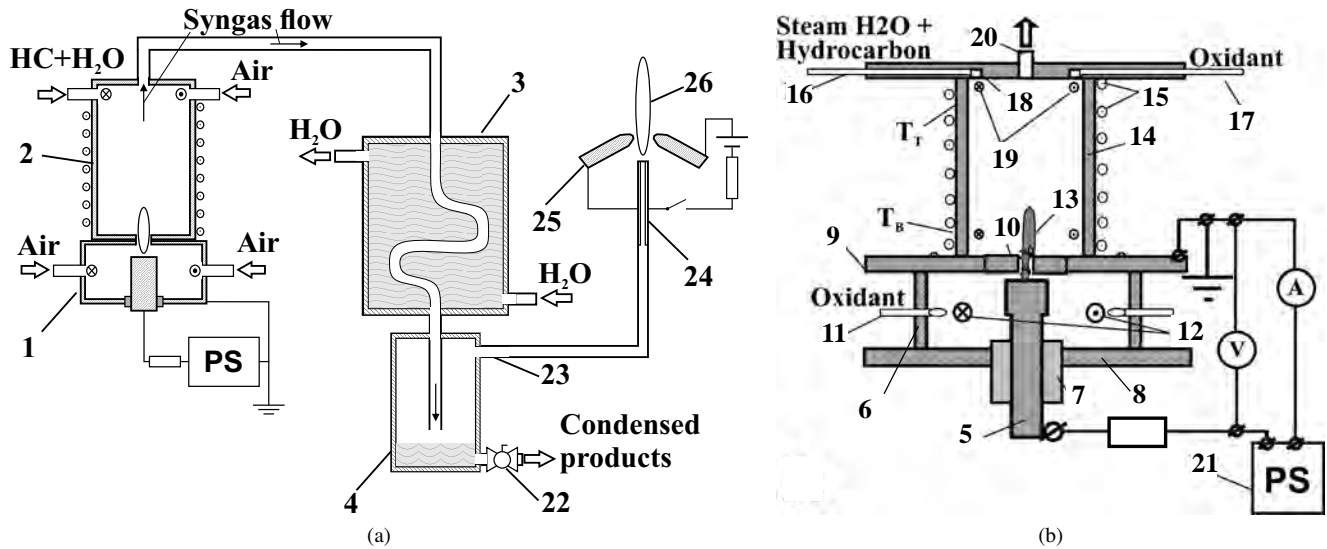
Fig. 1. Schematic representation of (a) experimental setup and (b) plasma system with rotating gliding discharge and solid electrodes: 1 – discharge chamber, 2 – reaction chamber, 3 – cooler, 4 – condenser, 5 – HV electrode/anode, 6 – metal wall of discharge chamber, 7 – ceramic sleeve, 8 – metal flange, 9 – grounded metal flange/cathode, 10 – stainless steel sleeve, 11,12 – oxidant injection channels, 12 – direction of vortex flow, 13 – plasma torch, 14 – reaction chamber wall, 15 – external heater, 16 – hydrocarbon injection channel, 17 – oxidant injection channel, 18 – channel for directing flow, 19 – direction of vortex flow, 20 – exit for reforming products, 22 – valve, 23 – fluorocarbon tube, 24 – metal nozzle, 25 – transverse discharge, 26 – syngas flame

consisted of the system for the reforming of hydrocarbon into syngas, systems for syngas cooling and condensed liquid collection, and a syngas combustion system (Fig. 1a).

The reforming system consisted of a discharge chamber (1) with low-power rotating gliding discharge with solid electrodes and a reaction chamber with an external heater (2). The combustion of syngas was done in the open airspace and was sustained by the plasma of transverse DC discharge (23-25). Both discharge and reaction chambers (Fig. 1b) are made of stainless steel and have cylindrical shape. The reforming system does not have water-cooling, thus it is possible to avoid large temperature gradients along the wall of the reaction chamber.

The discharge chamber is 90 mm in diameter and 35 mm in height. Lower and upper parts of the reaction chamber are tightly closed with metal flanges. Cylindrical T-shaped electrode (5) is introduced into the discharge chamber (6) through a dielectric ceramic sleeve (7) located at the lower metal flange (8) aperture. This electrode is under high potential and used as an anode. The inter-electrode distance can be changed by moving the anode along the chamber axis. The upper metal flange (9) is grounded and used as a cathode. Both electrodes are made of stainless steel.

The initial distance between two electrodes is 1.5 mm. The upper metal flange (9) has a stainless-steel sleeve (10) placed in the center. The center of the sleeve (10) has an aperture with a 3.5 mm nozzle inserted in it. One end of the discharge channel glides along the surface of the nozzle and the upper flange (9). Oxidant flow is injected through a channel (11) of 4 mm in diameter with a speed of 19.9 m/s, tangent to the sidewall of the discharge chamber (6), forming clockwise vortex flow (12). A plasma torch (13) is introduced into the reaction chamber (14), which temperature can be maintained in the range of 100 – 900 $^o$C by either a heating element (15)

or the complete combustion of a part of the hydrocarbon.

The temperature of reaction chamber outer wall (Fig. 1b-14) at both top ($T_T$) and bottom ($T_B$) is measured by two thermocouples. The mixture of hydrocarbons and distilled water steam is introduced through a channel (16) and oxidant is introduced through 4 mm channel (17) with a velocity of 5.7 m/s, both tangentially to the sidewall of the reaction chamber and along a channel (18), forming a "tornado"-type [23] reverse vortex flow (19). The rotating mixture of hydrocarbons, water steam and oxidant moves to the bottom of the reaction chamber and towards its central axis. The plasma-activated oxidant, which is injected into the reaction chamber along its axis, interacts with the hydrocarbon-containing mixture and initiates reforming. Reforming products move upwards toward the exit from the reaction chamber. The reaction chamber height is 100 mm and its diameter is 42 mm.

Syngas exits the reaction chamber through a channel of 6 mm in diameter (20) and enters a cooler (3). The cooler comprises a 1 m long stainless steel pipe with the inner diameter of 6 mm, which is submerged in 1 L of flowing water at room temperature. There is a condenser (4) installed at the cooler outlet to collect condensed liquid. The condensed liquid can be gathered through a valve (22), but it has not been analyzed for the operating modes presented is this paper. The temperature of cooled gaseous reforming products after they leave the cooler is no more than 30 $^o$C. Syngas flow at the cooler output has been measured by the rotameters (Dwyer RMA-22-SSV and RMA-23-SSV) with $\pm 4\%$ accuracy.

Gas chromatography results showed that the density of gas obtained during reforming is approximately 10 % lower than the air density. To compensate for the density difference, obtained flow rates of produced gas were multiplied by 1.05 – a correction factor calculated per [28]. Standard 0.5 L glass flasks have been used to sample syngas for the analysis
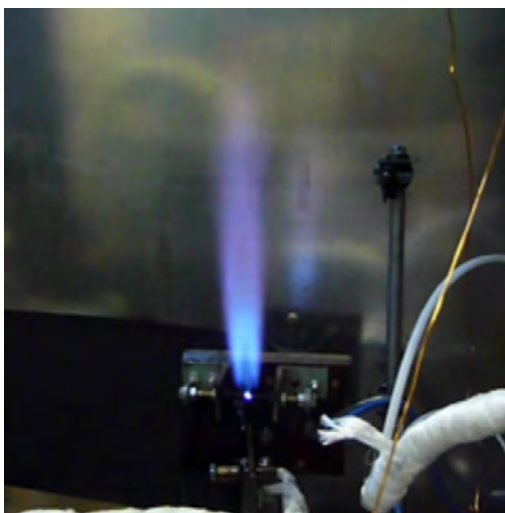
Fig. 2. Open air combustion of syngas ($\approx$10 kW) in the air, supported by the transverse DC discharge ($\approx$25 W).

of its composition using mass spectrometer and gas chromatograph. Gas chromatography has been performed using Agilent 6890 N gas chromatograph with separate columns for the detection of light gases and hydrocarbons, which has $< 0.1\,\%$ measurement error.
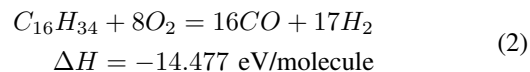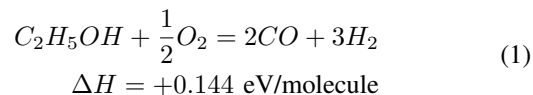
Obtained syngas left the system through a fluorocarbon tube (23) and was supplied to a combustion device. Produced gas was burned to avoid syngas accumulation and ensure its safe disposal, allowing the system to operate continuously for a long period of time. Syngas was combusted in the open air, using a metal nozzle (24) which released produced gas into the plasma channel of a transverse discharge (25). Additionally, syngas was combusted in the standard Navien Ace-20K and Aston OM-W42(10L) water heaters, which are designed to burn natural or liquefied petroleum gas.

The BP-100 DC power supplies (21) with an open circuit voltage of $7\,$kV were used in both discharge circuits. With the ballast resistance of $4 - 120\,$kOhm, the current of stable discharge is $20 - 400\,$mA. Reforming of the model hydrocarbons has been conducted at the current of $75\,$mA and voltage of $0.9\,$kV. During the hybrid plasma-catalytic reforming of hydrocarbons, the temperature of the reaction chamber was maintained in $450 - 500\,^oC$ range. There were two ways to preheat the reaction chamber: using the external heating element or doing the complete combustion of ethanol in the reaction chamber.

The preheating of the system using $300\,$W external heating elements took $45$ minutes. The system heating time when using ethanol combustion, which is equal to the power of $2\,$kW, maintained by the discharge in the reaction chamber was 10 minutes. After the reforming chamber has been heated to the required temperature, external heating was turned off and hydrocarbon reforming was initiated. The syngas samples for the gas chromatography were gathered 5 minutes after the start of hydrocarbons reforming process.

Sunflower oil ($C_{17}H_{33}COOH$) and ethanol ($C_2H_5OH$) have been used as model oxygen-containing hydrocarbons and

diesel fuel ($C_{16}H_{34}$) has been used as model hydrocarbon without oxygen. Air has been used as the model oxidant. In further calculations, the chemical composition of diesel was considered being identical to hexadecane ($C_{16}H_{34}$), which is often used as a substitute for diesel fuel [30]. Air and hydrocarbon flows have been chosen to match the stoichiometry of the partial oxidation reactions. Examples of these reactions for ethanol and diesel with corresponding enthalpy changes $\Delta H$ are as follows:

$$C_2H_5OH + \frac{1}{2}O_2 = 2CO + 3H_2 \tag{1}$$
$$\Delta H = +0.144 \text{ eV/molecule}$$

$$C_{16}H_{34} + 8O_2 = 16CO + 17H_2 \tag{2}$$
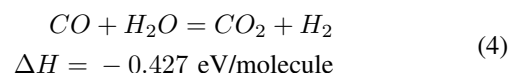$$\Delta H = -14.477 \text{ eV/molecule}$$

Diesel fuel and sunflower oil were introduced into the reaction chamber mixed with overheated water steam. The addition of the overheated steam reduces the amount of soot and assists the introduction of hydrocarbons into the reactor considering their high boiling points and high viscosity.

Soot removal occurs due to the reaction:

$$C + H_2O = CO + H_2 \tag{3}$$
$$\Delta H = +1.361 \text{ eV/molecule}$$
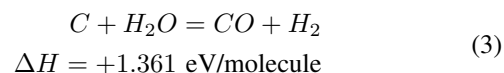
Water gas shift reaction is possible due to $H_2O$ presence:

$$CO + H_2O = CO_2 + H_2 \tag{4}$$
$$\Delta H = -0.427 \text{ eV/molecule}$$

All characteristic parameters of the chemical substances and reactions used in this research have been obtained from the NIST database.

## III. Results

Different $H_2$/CO ratios of syngas are required for different applications. For example, $H_2$/CO ratio of 2/1 is needed to synthesize methanol, and 1/1 to synthesize acetic acid or methyl formate [31]. The fuel cells need as much $H_2$ in syngas as possible. If the syngas is needed to generate heat, the mixture of $H_2$ and CO with light $C_xH_y$ is suitable.

Fig. 3 shows the flames of open air combustion of syngas, which was produced from diesel fuel, sunflower oil, and ethanol. Diesel fuel, sunflower oil and ethanol have been introduced in the amounts equal to the power of $5\,$kW, which releases at their full combustion. The resulted diesel fuel flow was $7.3\pm0.36\,$mL/min, sunflower oil flow was $9.1\pm0.45\,$mL/min and ethanol flow was $13.5\pm0.4\,$mL/min. The temperature of injected hydrocarbons was $25\,^oC$. The flow of distilled water steam has been selected to fit the optimal mode of operation in terms of reforming efficiency. The needed amount equals to the half of the amount of water that is necessary for the reaction stoichiometry in order for all CO to be substituted with $H_2$ and $CO_2$ in the case of diesel. This condition is satisfied by $4.4\pm0.22\,$g/min flow of water steam. The same water steam flow has been introduced in the cases of sunflower oil and ethanol as in the case of diesel fuel. The flow of injected air was $\approx 25\,$L/min in the cases of diesel fuel and sunflower oil and $12.5\,$L/min in the case of
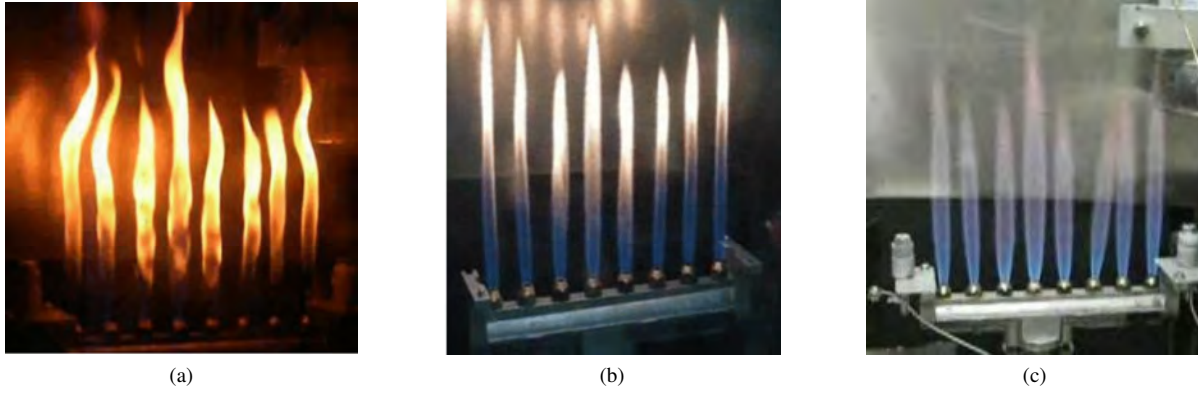
Fig. 3. Photos of the flames of open combustion of syngas produced from (a) diesel fuel, (b) sunflower oil, and (c) ethanol.

TABLE I
THE COMPONENTS (% OF VOLUMETRIC) OF SYNGAS PRODUCED DURING PLASMA-CATALYTIC REFORMING OF DIESEL FUEL AND ETHANOL.

| | $H_2$ | CO | $CH_4$ | $C_2H_4$ | $C_2H_2$ | $C_2H_6$ | $C_3H_6$ | $C_3H_8$ | $iC_4H_{10}$ | $nC_4H_{10}$ | $N_2$ | $CO_2$ | $H_2O$ | $O_2$ | $C_2H_5OH$ | $C_{16}H_{34}$ | $\sum$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Diesel fuel | 3.55 | 0.00 | 0.00 | 3.85 | 1.19 | 0.24 | 0.91 | 0.00 | 0.32 | 0.31 | 75.62 | 8.89 | 2.33 | 2.79 | 0.00 | 0.00 | 100 |
| Ethanol | 14.01 | 16.29 | 12.17 | 4.49 | 0.80 | 1.09 | 0.11 | 0.09 | 0.12 | 0.05 | 44.79 | 4.19 | 1.51 | 0.00 | 0.29 | 0.00 | 100 |

ethanol. The same air flow has been introduced in the case of sunflower oil as in the case of diesel fuel because sunflower oil has approximately the same amount of carbon atoms not bound with oxygen atoms (17 atoms per molecule) as diesel fuel (16 atoms per molecule). The temperature of injected steam was $\approx 250\,^{o}$C and the temperature of the air was $25\,^{o}$C. The reaction chamber temperatures were $T_T = 500\,^{o}$C and $T_B = 480\,^{o}$C. The flame of syngas produced during the plasma-catalytic reforming of sunflower oil (Fig. 3b) and ethanol (Fig. 3c) are more stable during the combustion and contain much less soot than the flame of syngas produced from the diesel fuel at the same conditions (Fig. 3a). We did not conduct the analysis of the soot formation in the reaction chamber during this study.

Table I shows the main components of syngas formed during the plasma-catalytic reforming of diesel fuel and ethanol. Diesel fuel and ethanol have been introduced in the amounts equal to the power of $2\,$kW, which releases at their full combustion. Resulted ethanol flow was $5.4\pm0.2\,$mL/min and diesel fuel flow was $3.4\pm0.2\,$mL/min. The temperature of injected hydrocarbons was $25\,^{o}$C. The flow of the distilled water steam has been selected to fit the optimal mode of operation in terms of reforming efficiency. Required amount equals to a half of the amount of water that is necessary for the reaction stoichiometry for all CO to be substituted with $H_2$ and $CO_2$. The flow of water steam was $1.7\pm0.1\,$mL/min in the case of ethanol and $1.8\pm0.1\,$mL/min in the case of diesel. The flow of injected air was $5\,$L/min in the case of ethanol and $10\,$L/min in the case of diesel. The temperature of injected steam was $\approx 250\,^{o}$C and the temperature of the air was $25\,^{o}$C. Reaction chamber temperatures were $T_T = 500\,^{o}$C and $T_B = 480\,^{o}$C.

The amount of $N_2$ in reforming products is considered the same as in the reagents due to the absence of NO and $NO_2$ in the mass spectra of reforming products. Measurement error of the mass spectrometer that was used in this work is less than 1 %. We use the process of partial oxidation of hydrocarbons to produce syngas, and the energy needed to heat the reagents to the desired temperature is taken from the exothermal reactions that occur inside the reactor. $CO_2$ is always present in the reforming products, probably as the product of water gas shift reaction, complete oxidation of hydrocarbon or oxidation of CO.

There has been no CO observed in the cases of diesel fuel. This indicates that all produced CO reacted with introduced water in the reaction (4). Syngas produced from ethanol contains almost 4 times more hydrogen than syngas produced from diesel fuel, which explains the flame appearance on the photographs on Fig. 3. The amount of $CO_2$ is higher in the case of diesel fuel. A mixture of the reforming products presented in Table I contains $H_2$ and $CO_2$ but has no CO in the case of diesel. Further understanding of this fact needs additional study of the diesel fuel and ethanol conversion kinetics.

Under the assumption that the ratio between oxygen $O_2$ and nitrogen $N_2$ in the air is $\approx 1{:}4$, it turns out that in case of diesel fuel $\approx 14$ % of the oxygen from the initial amount did not interact. This may occur because of the various additives, which are added to commercial diesel fuel to offer better engine performance, fuel handling and stability, and increase contaminant control [29]. The $N_2$ volumetric fraction in the gas obtained during the diesel fuel conversion is approximately 1.7 times higher than in the gas obtained by the reforming of ethanol, which may be due to the presence of oxygen in the ethanol.

The theoretical yields of methanol and DME from $1\,$L of syngas produced during the plasma-catalytic reforming of diesel fuel and ethanol have been calculated. A mixture of $H_2$ and $CO_2$ can be converted, if necessary, into methanol and DME via the second stage of processing and under appropriate catalyst.

TABLE II
THE THEORETICAL POSSIBLE YIELD OF METHANOL AND DME FROM
1 L OF SYNGAS PRODUCED DURING PLASMA-CATALYTIC REFORMING OF
DIESEL FUEL AND ETHANOL.

| Syngas production feedstock | Diesel fuel | Ethanol |
|---|---|---|
| Hydrogen yield (g/L) | 0.0032 | 0.0125 |
| Methanol yield (g/L) | 0.0254 | 0.1000 |
| DME yield (g/L) | 0.0182 | 0.0718 |

Methanol can be synthesized from the produced gas mixture via the reactions with carbon dioxide:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad (5)$$

$$2CO_2 + 2H_2 \rightarrow CH_3OH + CO \quad (6)$$
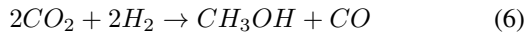
Reaction (6) uses less hydrogen and thus offers higher methanol yield. Based on this, reaction (6) was the one used for the calculation of the maximal theoretical yield of methanol from the conversion products. Two moles of hydrogen can yield one mole of methanol. DME can be produced from $H_2 + CO_2$ mixture or from methanol via reactions (7) and (8):

$$2CO_2 + 6H_2 \rightarrow CH_3OCH_3 + 3H_2O \quad (7)$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \quad (8)$$

Reaction (8) offers higher DME yield because of it has lower hydrogen consumption; therefore, it was used to calculate the maximal theoretical DME yield from produced gas. One mole of DME is produced from two moles of methanol. Using reactions (6) and (8) one mole of hydrogen can produce 0.5 moles of methanol or 0.25 moles of DME. Based on the hydrogen content in the synthesis gas (Table I) we can find the maximal theoretical yield of methanol and DME from one liter of produced synthesis gas. The actual yields of methanol and DME will be lower than the theoretical values and will significantly depend on the productivity of the catalyst used for reactions (6) and (8).

Table II holds the calculated values of methanol and DME yields in the case of converting 1 L of $H_2 + CO_2$ mixture without taking other components into account. Flammable components $C_2H_6$ and $C_2H_4$ cannot be converted to methanol and DME. They can be separated before the methanol/DME synthesis. Alternatively, they can be oxidized/carbonylated to oxygen-containing compounds such as $C_2$-alcohols or aldehydes, along with $H_2 + CO_2$ mixture during the second stage of processing. The calculation results presented in Table II show that the methanol and DME yield from 1 liter of syngas in the case of ethanol is 4 times greater than in the case of diesel fuel. Therefore, ethanol is more promising for the synthesis of liquid hydrocarbon.

Syngas produced from the ethanol (96 % ethyl alcohol) was used to determine the energy conversion efficiency of the standard water heater ($\eta_{heater}$) when using syngas as a fuel. $\eta_{heater}$ equals to a ratio between the change of the heat energy of water after passing the heater ($P_{water}$) and
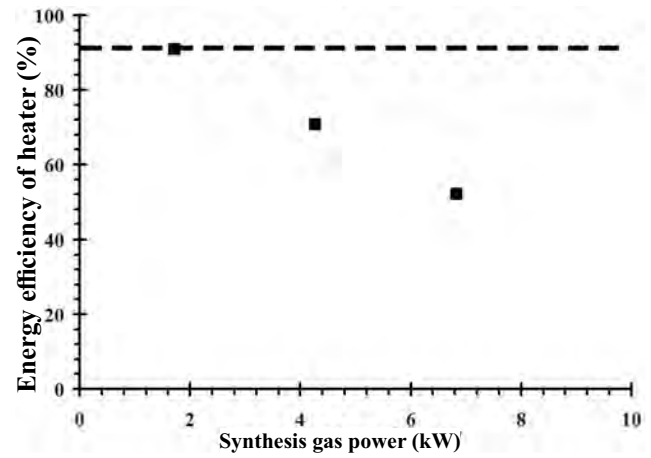


Fig. 4. Dependence of $\eta_{heater}$ during the combustion of syngas with turned off FD fan (markers); dashed line shows the value of $\eta_{heater}$ for the combustion of natural gas with turned on FD fan, which was provided in the water heater specification.

the chemical energy of syngas ($P_{syngas}$) calculated using gas chromatography:

$$\eta_{heater} = \frac{P_{water}}{P_{syngas}} * 100\% \quad (9)$$

The power (amount of energy in a unit of time) $P_{water}$ spent on heating the water is determined from the expression:

$$P_{water} = G_{water} \cdot \Delta T_{water} \cdot c_{water} \quad (10)$$

where $G_{water}$ is a water flow in L/min, $\Delta T_{water}$ is the increase of water temperature in the water heater, $c_{water}$ is the heat capacity of water. The temperature of the water was determined using the thermocouples.

The power released during the combustion of syngas $P_{syngas}$ (amount of heat released in a unit of time during the complete oxidation of the syngas in the combustion chamber of the water heater) is determined using:

$$P_{syngas} = G_{syngas} \cdot \sum_i Syngas_i \cdot LHV(Syngas_i) \quad (11)$$

where $G_{syngas}$ is the flow of syngas in L/min, $Syngas_i$ is the volumetric fraction of i-th syngas component, $LHV(Syngas_i)$ is the lower heating value of the unit of volume of i-th syngas component (the heat released during materials combustion without taking into account the heat released during the water condensation). The syngas composition was determined using gas chromatography.

Fig. 4 shows the common dependence of the energy conversion efficiency of the Navien water heater with turned off forced draft (FD) fan and with the nozzles for natural gas combustion on the syngas power $P_{syngas}$ calculated from (11).

The provided dependence shows that with the sufficient supply of air the efficiency of syngas combustion ($P_{syngas} = 1.7$ kW) is not lower than during the combustion of natural gas. The decreasing dependence of $\eta_{heater}$ on syngas power can be caused by the insufficient amount of air that is supplied to the water heater.
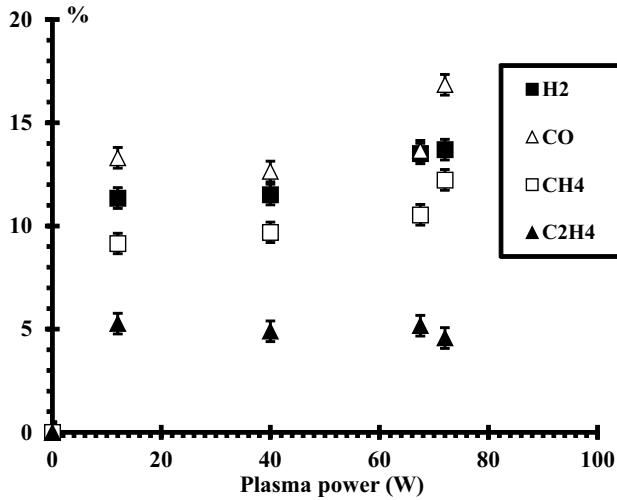
Fig. 5. Dependence of the composition of syngas obtained from 1296 mL/h ethanol flow which corresponds to 8 kW operation mode on the discharge power.

Reforming efficiency $\eta$ can be calculated using the lower heating values of syngas components and hydrocarbon [32], [33]:

$$\eta = \frac{G_{syngas} \cdot \sum_i Syngas_i \cdot LHV(Syngas_i)}{G_{HC} \cdot LHV(HC) + Plasma\ power} \cdot 100\% \quad (12)$$

where $LHV(Syngas_i)$ is the lower heating value of produced syngas components, $G_{HC}$ is the hydrocarbon flow, $LHV(HC)$ is the lower heating value of the hydrocarbon, *Plasma power* is the power consumption of electric discharge used for the plasma generation. $LHV(Syngas_i)$ that are used in our calculations consider only the LHVs of the gas-phase products and does not include the LHVs of the liquid condensed after the cooler, which is considered as an unreacted raw material. Further calculations showed that the efficiency of the system for hybrid plasma-catalytic reforming of ethanol is 87 %, which is significantly higher than 70 % obtained in similar studies [34]. The total amount of energy used for steam production during the experiment was less than $300\pm15$ W and did not depend on the composition and quantity of the raw materials. The addition of this value to the plasma power in the reforming efficiency equation (12) results in the reduction of $\eta$ from 87 % to 83 %. However, similar to other papers in the field, this decrease is not included in the calculations because it represents the efficiency of a steam generator and has no direct ties to the efficiency of the reforming system.

The ratio $\alpha$ between the chemical energy of produced syngas and the electric energy spent on plasma generation is calculated as follows:

$$\alpha = \frac{G_{syngas} \cdot \sum_i Syngas_i \cdot LHV(Syngas_i)}{Plasma\ power} \quad (13)$$

The ratio between the chemical energy of produced syngas and the electric energy spent on plasma generation is $\alpha = 70$ for plasma-catalytic reforming of sunflower oil (in 5 kW mode). The calculation of $\alpha$ for ethanol in the same mode gives the value of $\alpha = 60$.

It is clear from the equations (8) and (9) that the reforming efficiency ($\eta$) and the ratio between the chemical energy of produced syngas and the electric energy spent on plasma generation ($\alpha$) depend on electrical energy put into the discharge that generates plasma (Plasma power). A study of $\eta$ and $\alpha$ dependences on the discharge power in the plasma generator has been conducted. During the study, the input ethanol flow was 1296 mL/h and corresponded to 8 kW operation mode.

Fig. 5 shows the change in the composition of obtained syngas depending on the discharge power for the modes used for the determination of $\alpha$ and $\eta$.

Gas chromatography did not detect oxygen in the collected samples of the ethanol reforming products. The high amount of CO compared to the syngas from diesel fuel and sunflower oil comes from the lack of reaction (4) due to the small amount of water in the reagents.

The response time of the reforming process on the state of the discharge was determined from the visual observations of the flames of combusted syngas. The disappearance and appearance of the flame have been considered as the marks of the stop and start of the reforming process. For all studied values of discharge power, the discharge shutdown caused almost immediate (in less than 5 seconds) stop of the reforming process, which led to the disappearance of the gaseous products and condensation of all raw material introduced into the system in the condenser. The time between the start of discharge and the start of reforming was less than 4 seconds. The syngas residence time in the gas line between the reactor and the combustion device is approximately 2-3 seconds.

Syngas composition shows no significant change with the change of discharge power. Reforming did not occur with the discharge turned off. During the plasma reforming, the hydrocarbons are blown through discharge together with the oxidant and the change in discharge power significantly affects the syngas composition [18], [35]. In our case, the plasma-catalytic reforming of hydrocarbons was conducted and only a part of oxidant is blown through discharge while the hydrocarbon is introduced into the reaction chamber along with the rest of the oxidant. However, the discharge power significantly affects the ratio between the chemical energy of the produced syngas and the electric energy spent on the plasma generation and the reforming efficiency.

The calculated values of $\eta$ and $\alpha$ (see Fig. 6) show the sharp increase of the ratio between the chemical energy of produced syngas and the electric energy spent on plasma generation with the decrease of discharge power. However, the reforming efficiency is reduced at the same time. Therefore, the optimal studied mode of ethanol plasma-catalytic reforming is at $\eta \geq 85\%$ and $\alpha \approx 100$. Fig. 6 shows, that $\alpha \approx 100$ when $\eta \approx 80\%$, which makes the studied system competitive with other existing analogues. For the operating modes with $\alpha \approx 100$, the energy yield of hydrogen is $\approx 300$ g(H$_2$)/kWh, which is higher than the known values for plasma reforming [36]. Plasma-catalytic reforming of hydrocarbons makes possible the separate control of the syngas composition using the reaction chamber parameters and of the ratio between the chemical energy of the produced syngas and the electric energy spent on the plasma generation and the reforming efficiency
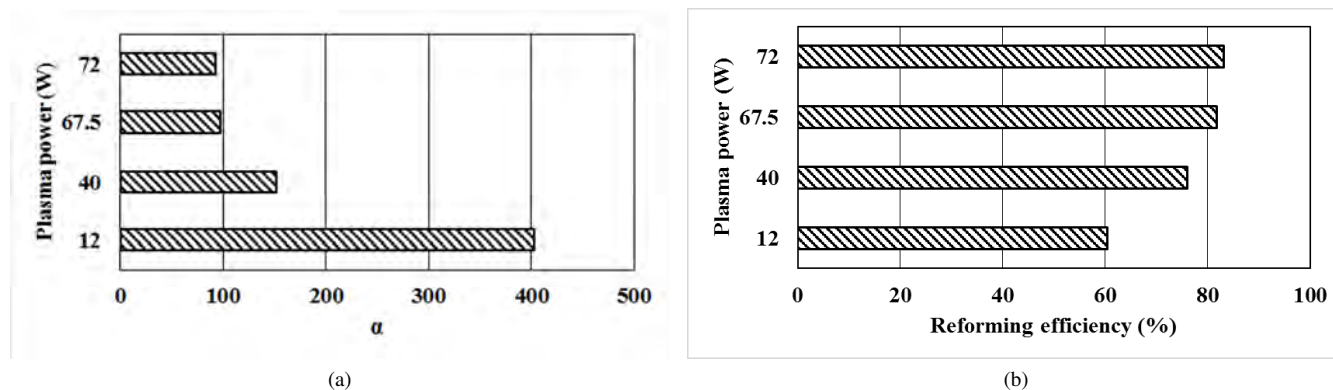
(a)                                                     (b)

Fig. 6.   Dependence of the ratio between the chemical energy of the produced syngas and the electric energy spent on the plasma generation ($\alpha$) and the reforming efficiency ($\eta$) on discharge power during 1296 mL/h ethanol flow, which corresponds to 8 kW operating mode.
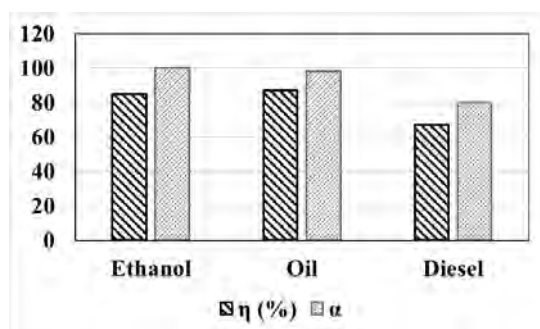


Fig. 7.   Dependence of $\alpha$ and $\eta$ on the raw materials (ethanol, sunflower oil, diesel fuel) for the reforming conducted in 8 kW operation mode.

using the discharge power.

Fig. 7 shows the values of the ratio between the chemical energy of produced syngas and the electric energy spent on plasma generation ($\alpha$) and the reforming efficiency ($\eta$) during the reforming of different raw materials (ethanol, sunflower oil, diesel fuel) in 8 kW operation mode.

As seen from the provided dependencies, the ratio between the chemical energy of produced syngas and the electric energy spent on plasma generation and the reforming efficiency values show the prospects of using plasma-catalytic reforming systems with rotating gliding discharge in industrial processes.

## IV. CONCLUSION

The investigation of plasma-catalytic reforming of the liquid oxygen-containing hydrocarbons from the renewable raw materials and of the hydrocarbon without oxygen showed that it has high reforming efficiency and a high ratio between the chemical energy of the produced syngas and the electric energy spent on the plasma generation.

The research proves the possibility of using syngas produced from the renewable raw materials in standard water heaters designed for the combustion of natural and liquefied petroleum gas.

The plasma-catalytic reforming features quick response of the reforming process to the change of the state of discharge. This allows the high level of control over the operation of the reforming systems.

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