

Short communication

Hydrogen production by reforming of hydrocarbons and alcohols in a dielectric barrier discharge[☆]

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Abstract

This work reports about the use of plasmas to obtain hydrogen by reforming of hydrocarbons or alcohols in mixtures with CO₂ or H₂O. The plasma is activated in a dielectric barrier discharge (DBD) reactor working at atmospheric pressure and low temperatures (i.e., about 100 °C). The reactor presents a great versatility in operation and a low manufacturing cost. Results are presented for the reforming of methane, methanol and ethanol. Methane transforms up to a 70% into CO and H₂ without formation of any kind of superior hydrocarbon. For the two alcohols 100% conversion into the same products is found for flows much higher than in the case of methane. The work reports a description of the reactor and the operational conditions of the power supply enabling the ignition of the plasma and its steady state operation.

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1. Introduction

Fuel cells are currently considered as one of the most efficient procedures of energy production [1]. Their high efficiency, together with their low level of pollutant emissions justify the enormous effort made during the last years for their practical implementation. However, one of the major difficulties for their definitive commercial implementation, especially as mobile sources, is the handling of the hydrogen required for their use. Thus, serious problems must still be solved to get a practical way for the storing and transportation of this fuel. An alternative is the “in situ” production of hydrogen utilizing fuels such as gasoline, natural gas or alcohols [2].

Steam reforming of methane (SRM) and water electrolysis are generally considered as the most straightforward methods to obtain this fuel [3]. More recently, the use of plasmas has been proposed as a feasible alternative particularly interesting for its use in mobile sources [4]. The present paper reports a preliminary description of the construction and operation of a plasma

reactor based on a dielectric barrier discharge (DBD) for the reforming of hydrocarbons and alcohols. It works at atmospheric pressure and low temperature under non-equilibrium conditions. DBD discharges provide much flexibility with respect to the geometrical shape and operational parameters of the reactor as well as with regard of the type of gas mixture utilized. Generally, the scaling-up of this type of reactors to large dimensions is straightforward. Although DBD has been used previously for the treatment of gases [5], it is still necessary a systematic study of the influence of the different working parameters on the reaction yield. In the present work, we present the description of a DBD reactor and some operational results for the reforming of mixtures of a fuel (methane, methanol and ethanol) with CO₂ or H₂O. An assessment of the influence of the type of gas mixture, parameters such as voltage and frequency or even the porosity of the surfaces sustaining the plasma is also addressed in this paper.

2. Experimental

The experimental arrangement used for the study is shown in Fig. 1. It consists of the following parts as depicted in this figure: (1) A stainless steel cylinder with controlled roughness in the zone of the plasma discharge. This roughness was produced

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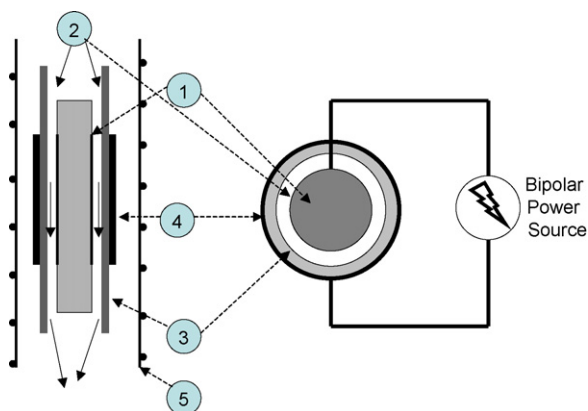


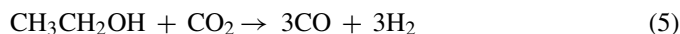
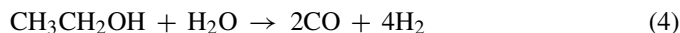
Fig. 1. Scheme of the experimental DBD setup. The different parts of the reactors are described in the text.

by sand blasting and consisted of 1 μm depth irregularities. (2) Entry and circulation of gases. (3) An alumina or quartz tube acting as dielectric barrier. This quartz/alumina tube has an outer diameter of 25 mm and a wall thickness of 2 mm. (4) A metal electrode made of stainless steel that covers externally the dielectric tube. The area covered by this external electrode defines the zone where the plasma is produced. (5) An external furnace to maintain the reactor at temperatures higher than 110 $^{\circ}\text{C}$ to avoid condensation of water. A critical parameter of the production of plasma inside the reactor is the distance between the rough surface of the inner stainless steel cylinder and the dielectric tube. This distance lies between 1 and 3 mm. Total volume of the empty space in the reactor was between 7 and 15 cm^3 .

An ac power supply whose voltage could be varied between 10 and 30 kV and its frequency between 1 and 6 kHz was used to ignite the plasma. The power source had a bipolar configuration with two electric transformers in the output. Each transformer provides a maximum voltage of 15 kV. This architecture gives remarkable characteristics to the discharge so that filaments occur not only at the rising edge but also at the falling edge of applied voltage. The electrical characterization of the source was made with a digital oscilloscope (TEKTRONIX TDS3034B).

Gas mixtures consisting of defined amounts of CH_4 plus CO_2 or H_2O , CH_3OH or $\text{CH}_3\text{CH}_2\text{OH}$ plus CO_2 or H_2O are introduced in the reactor. The proportion of the gas mixtures are adjusted by mass flow controllers according to the following

stoichiometries of the expected reactions:



Generally, a slight excess of CO_2 or H_2O was added to the mixture to avoid that soot particles form because of the direct dissociation of the hydrocarbon or alcohols. The gas line was heated at around 110 $^{\circ}\text{C}$ to avoid any condensation of water. The reaction products were analyzed with a mass spectrometer (SENSORLAB) placed downstream the reactor. This mass spectrometer was carefully calibrated with mixtures of the pure gases to quantify the reaction efficiency for all experimental conditions.

The reaction efficiency has been controlled as a function of the applied voltage and frequency of the applied discharge and the flow of reactants. The evolution of the voltage and the current in the reactor under working conditions was determined by means of an oscilloscope connected to the power source output through a high voltage probe and a coil (Pearson Electronics), respectively.

3. Results and discussion

The reaction processes occurring in our experimental set-up adjusted to the stoichiometries given by Eqs. (1)–(5). This means that no higher hydrocarbons were formed during the reforming of the fuels, CO and H_2 being the majority reaction products of the process. This is a general behavior found for similar plasma reactions induced by DBD discharges [6]. The reaction yield was different depending on the reaction and the total flow of reactants. Fig. 2 shows the evolution of the conversion yield as a function of the total flow of reactants for mixtures of the three fuels with CO_2 . Similar results were obtained when H_2O was used as the other reactant instead of CO_2 . These plots were obtained for a total voltage of 30 kV and a frequency of 3.2 kHz. The decrease in conversion yield found as the total flow increases indicates that the residence time of the reactants in the plasma zone is a critical parameter for the control

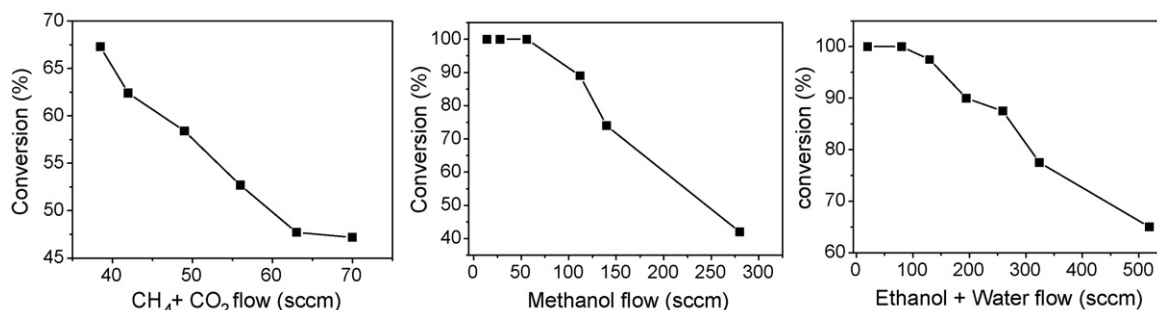


Fig. 2. Evolution of the conversion yield of the fuels as a function of the total flow of gases for mixtures of increasing amounts of CH_4 with 35 sccm of CO_2 (left), methanol (middle) and mixtures of ethanol with H_2O in a ratio 2:1 (right). The X and Y scales in the three panels are different.

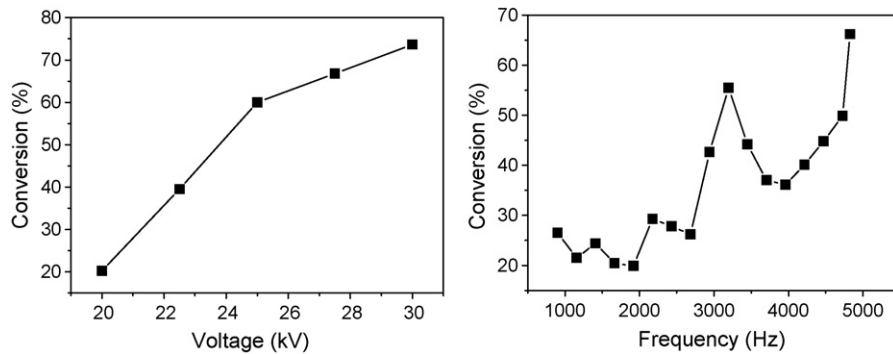


Fig. 3. Evolution of the conversion yield of CH_4 for mixtures $\text{CH}_4 + \text{CO}_2$ (3.5 sccm of CH_4 and 7 sccm of CO_2) as a function of the applied voltage for a frequency of 4 kHz (left) and as a function of the frequency for an applied voltage of 15 kV (right).

of the reaction efficiency. It is also evident from the plots in this figure that the plasma reaction is less efficient according to $\text{CH}_4 < \text{CH}_3\text{OH} \sim \text{CH}_3\text{CH}_2\text{OH}$. This tendency agrees with the high kinetic stability of the CH_4 molecules [7]. CH_3OH decomposes in its totality into CO and H_2 (i.e., reaction (3)) without mixing with either water or CO_2 . For CH_3OH and $\text{CH}_3\text{CH}_2\text{OH}$, total decomposition can be achieved for flow values up to 60 and $90 \text{ cm}^3 \text{ min}^{-1}$ (sccm), respectively. Taken into account the total free volume of the active zone of the reactor (i.e., 10 cm^3 for an electrode separation of 2 mm), these maximum flows for the two alcohols yield 0.2 and 0.6 cm^3 of hydrogen per second and unit volume of the reactor. Since the scaling of the experimental conditions is rather straightforward with this type of DBD reactors, these figures of production of hydrogen can be used as targets to assess the efficiency of big-size reactors directly supplying hydrogen to fuel cells and/or any other kind of real installations.

The reaction yield was also very much dependent on the roughness of the inner stainless steel tube (designed with 1) in the scheme of Fig. 1) and it decreased when using a flat tube where no roughness was artificially created by sand blasting.

Investigations were also carried out to determine the influence of the electrical variables of the process, i.e., the voltage and the frequency of the applied electrical discharge. The obtained results are reported in Fig. 3 for CH_4 as a fuel. Similar curves were obtained for the two alcohols investigated in this work. From these figures, it is apparent that the conversion yield increases with the applied voltage, although at very low voltages the curve tends to reach a steady state value (not yet reached in Fig. 3). The evolution with frequency presents a relative com-

plex evolution, with the appearance of two conversion maxima at frequencies of 3200 and 5000 Hz. The inspection of the type of discharge at different values of frequency revealed that for the values of these two maxima the discharge had a diffuse character, while for the other of values the discharge was filamentous. A general tendency deduced from the plots in Fig. 3 is the increase of conversion efficiency with the operating frequency and the applied voltage. In parallel, by analyzing the electrical signals provided by the used ac power supply, it could be determined that the power density applied to the DBD plasma and the space–time duty ratio (the time per second that the pulsed power is applied) increased with both the applied voltage and operating frequency. The different regimes of the discharge are clearly evidenced in Fig. 4 representing the form of the voltage and current curves at frequencies where either continuous or filamentary discharges are produced. It is apparent in these plots that for frequency values yielding a continuous discharge (e.g., at 4300 Hz) the voltage and the current curves do not present any sharp change indicative of the existence of sparks or filaments. By contrast, for the filamentary discharge (e.g., at 5800 Hz) the current curves depict sharp peaks superimposed on the sinusoidal curve that are indicative of the formation of filaments. These filaments are generally formed when the positive or negative voltages produced by the bipolar power source induces a local electric field strength that reaches the ignition level of the gas and produces the electrical breakdown at many points of the surface of the reactor. This behavior has been previously reported for other type of processes based on DBD discharges [8]. Calculations of the energy consumed in the discharge yields that 1 mol of hydrogen

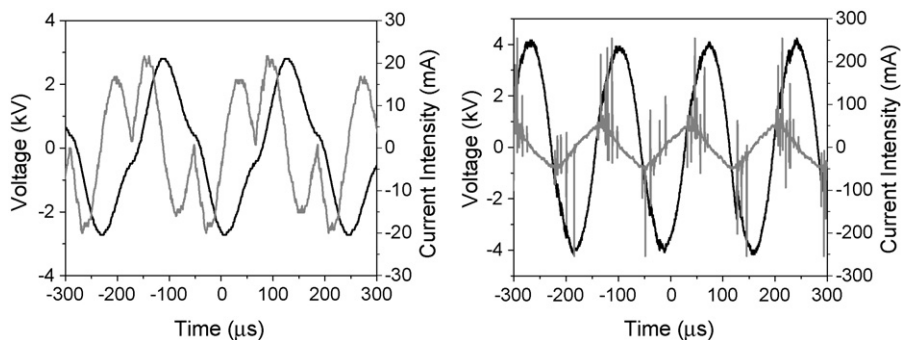


Fig. 4. Plots of the voltage (black line) and current (gray line) waveforms for continuous (left) and filamentary (right) discharges at respectively, 4300 and 5800 Hz.

can be produced in our reactor by using an energy of approximately 4, 0.6 and 0.3 kWh for, respectively CH₄, CH₃OH and CH₃CH₂OH as a fuel.

4. Conclusions

This preliminary work dealing with the use of DBD discharges for the reforming of fuels has evidenced that this process is a feasible technology which, depending on the operational conditions and type of fuel, is able to yield very high conversion rates. For methanol and ethanol 100% conversion can be obtained for relatively high flows of reactants. The applied voltage and the operational frequency are also very important parameters for the control of the process. Thus, increasing the voltage always produced an increase in the conversion yields. By contrast, the conversion yield as a function of frequency describes a complex profile that is attributed to a change in the conditions of the plasma from continuous to filamentary. Although the reasons for such a behavior still need to be investigated, it has been demonstrated that the control of this parameter is critical for the optimization of the reaction yield. A final remark refers to the roughness of the surfaces sustaining the discharge. Our results show that a controlled roughness, rather than the porosity as previously claimed [9], is very important for the optimization of the process.

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