Ethanol decomposition routes by an atmospheric pressure microwave plasma torch: towards the eco-friendly production of hydrogen

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Abstract: The decomposition of ethanol by an Ar TIAGO torch plasma opened to the atmosphere to produce hydrogen is researched. Two different routes are found which are related to the influence of the surrounding air, affecting to plasma species and gas temperature, but also to by-products formation at the plasma exit. It has been found that high-temperature plasmas favour the production of hydrogen together with graphene by an eco-friendly process without the emission of greenhouse gases.

Keywords: hydrogen, graphene, atmospheric pressure, microwave, plasma

1. Introduction

Plasma technology has emerged as a useful technique for the decomposition of hydrocarbons or alcohols [1,2] for the formation of valuable by-products such as hydrogen or carbon-based nanostructures [2,3,4]. Among different plasma types, atmospheric pressure non-thermal plasmas, and more specifically those generated by a microwave torch, have been presented as the most suitable ones for this purpose because of (i) their capability of withstanding the introduction of substances and favouring the excitation and dissociation processes of molecules, (ii) the low power requirements and (iii) their suitability to be implemented at industrial level. Nevertheless, the decomposition process cannot be always considered as eco-friendly as desired since the target by-products are formed together with greenhouse gases [5]. Therefore, it is necessary to perform a thorough study concerning the exhaust gases in the decomposition process and the experimental conditions in which are produced. In this work, the experimental conditions for the green decomposition of an agricultural surplus such as ethanol (EtOH) for the formation of hydrogen and graphene by a microwave TIAGO torch plasma are researched.

2. Materials and Methods

The experimental set up was described in detail in [2]. Plasma was created by a TIAGO torch device and maintained by a power of 300 W supplied by a 2.45 GHz generator (SAIREM). High purity argon (99.999%) gas was used to initiate and feed the discharge with flows ranging from 0.15 to 1.5 L/min which were controlled by a HI-TEC controller (HI-TEC, Bronkhorst). Right after plasma ignition, different ethanol amounts (from 0.22 to 1 g/h) were added using a gas-phase liquid delivery system (CEM, Bronkhorst). To obtain simultaneous information on the processes taking place in the plasma and gaseous by-products obtained by ethanol plasma decomposition, two different analysis-techniques were utilized: Optical Emission Spectroscopy (OES) and Mass Spectrometry (MS). OES was used to study the formation of species and plasma kinetics with a 1-m focal length monochromator (Jobin-Yvon-Horiba) equipped with a 2400 grooves/mm diffraction grating and a CCD camera as radiation detector. The probe of a quadrupole mass spectrometer (QMS, PT M63 112, mod.Omnistar, Pfeifer Vacuum Technology) was utilized to analyse the composition of gases exiting the discharge. The mass spectrometer was previously calibrated to quantify hydrogen production. To prevent solid by-products from entering this device, a filter (re. 33127-201 from Iberfluid, Spain) was placed between the reactor and the spectrometer probe.

3. Results and Discussion

TIAGO torch plasma consists of a jet surrounded by a mixing layer. In this layer, the plasma gas interacts with the air surrounding the flame which highly affects plasma kinetics [6] and thus the decomposition process of ethanol [2].

To gain knowledge concerning plasma mechanisms which lead to the formation of different by-products, emission spectroscopy and mass spectrometry were jointly used. On the one hand, Figure 1 shows typical spectra emitted by TIAGO Ar/EtOH discharges when considering the same Ar flow and a small (0.22 g/h) or large (1.00 g/h) EtOH amounts. On the other hand, in Figure 2 it can be observed mass spectra obtained from the exhausting gas of these discharges compared to the gases when the plasma is switched off. Different species in the discharge as well as by-products (both solid and gaseous) were detected depending on both argon flow and ethanol amounts in the gas. The direct interaction of TIAGO discharges with the surrounding air affects the decomposition process of ethanol molecules.

As for the emission of molecular species coming from the discharges, CN (Cyanogen Violet System, $B^2\Sigma \rightarrow X^2\Pi$) is always formed due to the interaction of nitrogen with carbon atoms produced during the decomposition process. Nevertheless, C_2 emission (Swam System, $A^3\Pi_g \rightarrow X^3\Pi_u$) is only observed when either Ar or EtOH flows are large enough due to a reduced interaction of the

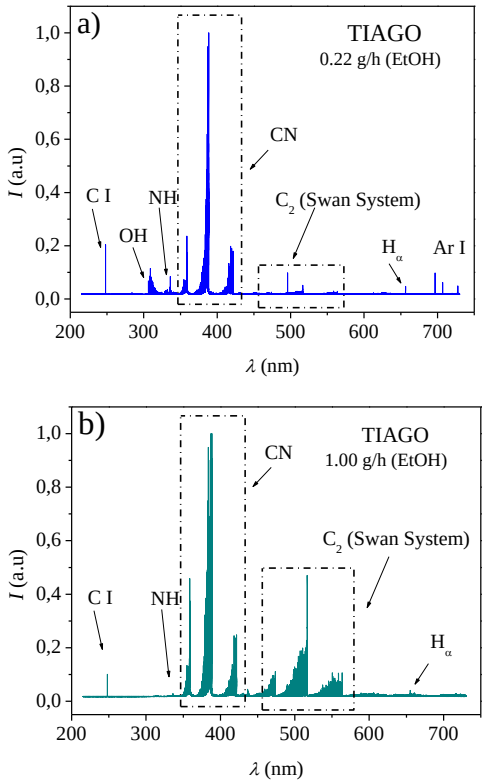

Fig. 1. Typical normalized spectra emitted by Ar/EtOH TIAGO discharges generated with 0.5 L/min of Ar and a) 0.22 g/h and b) 1.00 g/h of EtOH.

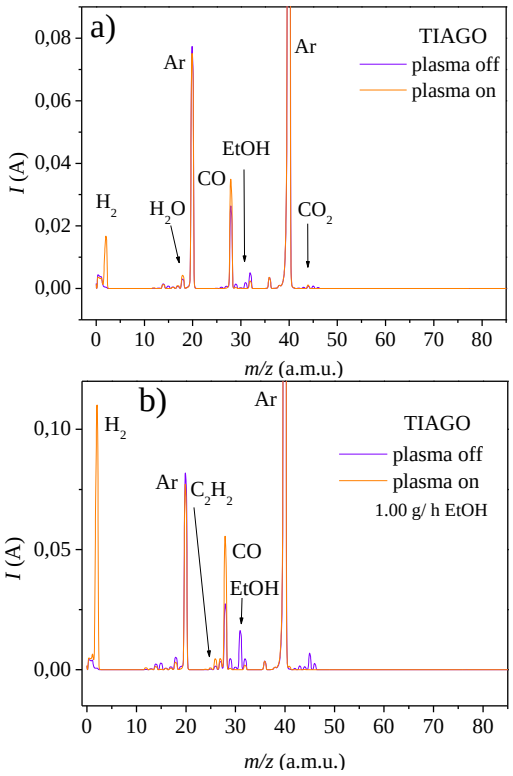

Fig. 2. Typical mass spectra from the exhaust gases of Ar/EtOH TIAGO discharges generated with 0.5 L/min of Ar and a) 0.22 g/h and b) 1.00 g/h of EtOH.

plasma jet with the air surrounding the discharge. Gas temperature was also affected by both flows. This plasma parameter is higher (>4500 K) in the cases of discharges sustained with large Ar or EtOH flows.

Moving to by-product formation, according to Figure 2, the main gaseous products at the plasma exit for low ethanol flows are H_2, H_2O, CO and CO_2, whereas for larger ones H_2 and CO are formed together with solid carbon identified as pure graphene [4]. This result is similar when keeping ethanol flow constant and increasing argon flow [2].

The presence of air components such as N_2 or O_2 is more presentative in the case of plasmas generated with small Ar [6] or EtOH flows [2]. Therefore, as a result, two different ethanol decomposition routes (Figure 3) are found which can be related to the influence of the surrounding air (oxygen availability): (i) an eco-friendly route when hydrogen and graphene are formed without the emission of CO_2 by a high-temperature (>4500 K) plasma process meanwhile (ii) a non-green route can be followed to produce hydrogen when ethanol is decomposed in low-temperature (<4500 K) with the emission of greenhouse gases.

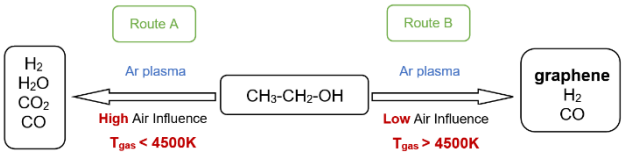

Fig. 3. Schematic representation of ethanol decomposition routes and by-products formation.

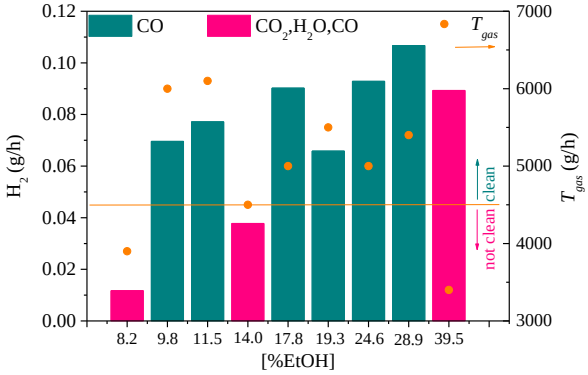

Fig. 4. Hydrogen production depending on ethanol concentration and gas temperature.

The production of hydrogen has been calculated in different experimental conditions. In figure 4, hydrogen production is presented versus the concentration of ethanol in the mixture in the left-y-axis. Ethanol concentration can be modified by varying either Ar gas or ethanol flows, which modifies the decomposition route. Besides, in the

right-y-axis of Figure 4, gas temperature is plotted versus ethanol concentration. As it can be observed, hydrogen production is not related neither to ethanol concentration in the plasma nor gas temperature. However, gas temperature affects the route to produce hydrogen, thus its production by a clean or not clean process. It is important to highlight that following a green hydrogen process, graphene is synthetized as well.

4. Conclusions

In this work, atmospheric pressure microwave discharges generated with a TIAGO torch were studied to obtain hydrogen from ethanol decomposition under several experimental conditions. Since TIAGO flames are sensitive to the air surrounding the discharge, there were found two different ethanol decomposition routes for hydrogen production.

The presence of air components (N_2 or O_2) in TIAGO plasmas influences the formation of plasmas species and plasma gas temperature. CN species are always formed but when plasma jet is effectively shielded from the entrance of air (either by increasing argon or ethanol flows), nitrogen availability is limited which favours the formation of C_2 species and the increase of plasma gas temperature. According to the analysis of the exhaust gases, two ethanol-chemistry decomposition routes can be described. On the one hand, with gas temperatures higher than 4500 K, ethanol is decomposed by a clean route producing syngas (H_2 and CO) and graphene as main by-products. On the other hand, lower plasmas temperatures favour H_2, H_2O, CO and CO_2 gas production from a non-eco-friendly route.

Acknowledgments

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