Chemical Engineering Journal 284 (2016) 1117–1126

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Experimental research on ethanol-chemistry decomposition routes in a microwave plasma torch for hydrogen production

R. Rincón [a,*], A. Marinas [b], J. Muñoz [a], C. Melero [a], M.D. Calzada [a]

[a] Laboratorio de Innovación en Plasmas, Edificio Einstein (C2), Campus de Rabanales, Universidad de Córdoba, 14071 Córdoba, Spain
[b] Departamento de Química Orgánica, Edificio Marie Curie (C3), Campus de Rabanales, Universidad de Córdoba, 14071 Córdoba, Spain

HIGHLIGHTS

- Hydrogen was produced in a clean process by atmospheric pressure TIAGO plasmas.
- Two ethanol-chemistry decomposition routes were found to produce hydrogen.
- Gas temperature was found a key parameter for ethanol decomposition process.
- Ar and ethanol flows influence both plasma species and by-products formation.
- Air ambiance alters plasma kinetics during the decomposition process.

ARTICLE INFO

Article history:
Received 29 April 2015
Received in revised form 3 September 2015
Accepted 11 September 2015
Available online 26 September 2015

Keywords:
Atmospheric-pressure plasma
Ethanol decomposition
Hydrogen production
Emission spectroscopy
Mass spectrometry

ABSTRACT

The study of ethanol decomposition process to produce hydrogen using an argon microwave plasma sustained by a Torche à Injection Axiale sur Guide d'Ondes opened to the atmosphere is presented. Different species in the discharge as well as by-products were detected depending on the amounts of both argon and ethanol flows used to sustain the discharge, which were related to the relative influence of air from the atmosphere surrounding the discharge. Furthermore, plasma gas temperature value was found to have a noticeable influence on ethanol decomposition chemistry; giving place to two different ethanol decomposition routes: (i) for higher temperatures (>4500 K), ethanol decomposition produced H_2, CO and carbon powder, whereas, (ii) at lower gas temperature (<4500 K), ethanol was mainly decomposed forming H_2, H_2O and CO with CO_2. These results indicate that the complete ethanol decomposition by means of a microwave plasma sustained with high gas temperatures results in the production of hydrogen through a clean and simple process.

1. Introduction

Plasma technology has been presented as a valuable catalytic-free technique for hydrogen production since plasma provides the necessary energy for the reforming of fuels, hydrocarbons or alcohols [1–3]. Among different plasma types, non-thermal ones are found to be the most appropriate for this purpose due to their low power requirements. Part of the energy supplied to the discharge is used to produce energetic electrons, providing energy for the generation of active species involved in the chemical reactions induced during the decomposition of the hydrogen source. In addition to hydrogen, plasma technology has been shown to be useful as a mean to produce the formation of valuable sub-products like petrochemical hydrocarbons [4] or carbon-based nanostructures such as carbon nanotubes [5,6] or graphene [6–9]. In particular, the possibility of working at atmospheric pressure makes plasma technology an economic and attractive technique for the implementation of the process on an industrial scale. Thus, it is not surprising that academia and industry have devoted resources and expertise to use non-thermal plasmas for the decomposition of hydrocarbons or alcohols to produce high valuable products.

In this sense, some non-thermal plasmas such as Dielectric Barrier Discharges (DBDs) have been successfully used to decompose alcohols like methanol [10,11] and ethanol [11–13] besides hydrocarbons [14,15] to obtain H_2 as well as light hydrocarbons. Additionally, in [2] natural gas was decomposed in a pulsed corona discharge and H_2, CH_4, C_2H_2, C_2H_4 and C_2H_6 by-products were obtained. Lindner et al. [16] reported the reforming of methanol into H_2, CO and H_2O within a DC microplasma reactor using N_2

* Corresponding author at: INRS-Énergie, Matériaux et Télécommunications, 1650 Boulevard Lionel Boulet, Varennes, Québec J3X-1S2, Canada.
E-mail address: rocio.rincon@emt.inrs.ca (R. Rincón).

http://dx.doi.org/10.1016/j.cej.2015.09.062
1385-8947/

as the carrier gas, whereas Aubry et al. [3] introduced a mixture of ethanol and water between two electrodes producing CO_2 in addition to H_2.

Notwithstanding the advantages of DBDs or corona discharge systems, microwave induced plasmas (MIPs) are presented as noteworthy electrodeless plasmas which can operate in a wide range of experimental conditions. Jasinski et al. [17–19] used a waveguide-based nozzleless cylinder-type microwave plasma source (MPS) at atmospheric pressure as a system to convert methane [17–19] and tetrafluoroethane [19] into hydrogen using both large amounts of hydrocarbon flows and high values of powers. In this case, a 100% of hydrogen selectivity was reported and carbon soot was formed on the reactor walls. Surface-Wave Discharges (SWDs), a special type of MIP, have also been researched for hydrogen production. Yanguas-Gil et al. [20] observed a complete decomposition of ethanol into H_2, CO and CO_2 as well as C_2 and higher hydrocarbons as trace levels in a SWD at reduced pressure. While a carbon deposition was noticed in the process, the addition of water avoided the soot formation. Wang et al. [21] detected the formation of radicals from alcohols (methanol, ethanol, propanol and butanol) decomposition giving rise to H_2, H_2O, CO and a mixture of hydrocarbons (mainly C_2H_2) also in a SWD at reduced pressure. Furthermore, Jiménez et al. [22] studied the decomposition of the aforementioned alcohols in an atmospheric-pressure SWD. Two different configurations were assessed: flame and column [23]. It was found that the flame configuration was the most appropriate to withstand the introduction of alcohols. For this configuration, the excitation processes inside the plasma were favoured by the high values of electron density and gas temperature [24,25]. In addition, in [26], hydrogen production (2.5 mole per mole of ethanol) together with CO and C_2H_2 as main gases using a SWD was reported. The same plasma source was successfully applied for the synthesis of multiwall carbon nanotubes and graphene [6] by the decomposition of ethanol.

Among other microwave sources, plasma torches are of special interest due to their capability of withstanding the introduction of substances and favouring excitation and dissociation processes of molecules. A continuous microwave power system has been used to produce a high conversion of methane [27,28] as well as methanol [29]. High H_2 and low C_2H_2, C_2H_4 and HCN selectivities were achieved using low power, together with the production of carbon nanoparticles, without the emission of CO_2 [27,28] from methane decomposition, contrary to what happened in the decomposition of methanol [29]. A surface wave driven torch operated in laminar [30] and vortex flows [31–34] was used to study the decomposition of ethanol [30,31,33,34], methanol [30–32] and propanol [31]. In [30], nearly a 100% decomposition of the hydrogen source was obtained, resulting in a high selectivity of H_2 and the formation of both CO and black carbon as by-products. Additionally, when water vapour was intentionally added to the alcohol, carbon soot formation was avoided while CO_2 was formed. Furthermore, in [31–34] a vortex flow configuration was assessed for hydrogen production. Although the same by-products were formed at the plasma exit, hydrogen production was increased. The experimental results agreed well with theoretical predictions for H_2 and CO production by means of the decomposition of ethanol [32], ethanol and water [34] and methanol [32]. In addition to the aforesaid plasma sources, TIAGO torch (*Torche à Injection Axiale sur guide D'Ondes*) has also been studied for this purpose [35]. Ethanol was almost completely decomposed (conversion rates higher than 99.6%) producing hydrogen with a high selectivity (up to 85%). In addition, it was shown that this plasma source withstands ethanol concentrations up to 7.5%. Besides, a high influence of the air ambience surrounding the discharge on the type of sub-products was found.

As it can be extracted from the results found with different plasma sources, alcohols or hydrocarbons can be effectively decomposed to produce hydrogen but, in addition, dissimilarities in the production of other gaseous products were also reported. According to the bibliography, the hydrogen-source can be decomposed to obtain H_2 and also, on the one hand, H_2O and CO_2 or, on the other hand, CO and light hydrocarbons. Therefore, studying and understanding the different decomposition routes as function of plasma operating conditions is crucial to enhance the production of hydrogen through a green process which avoids the formation of undesirable gases.

It is well-known that plasma processes (kinetics) can be modified by acting on the operating conditions. Hence, in the current work, the relationship between species produced from ethanol decomposition in the plasma generated by a TIAGO device and by-products formation at the plasma exit has been researched as function of operating conditions such as plasma gas flow and hydrogen-source amounts. With this study, we contribute to infer the dependence of plasma-ethanol decomposition process on the formation of products at the plasma exit, which results in a complete understanding of different chemical routes for ethanol decomposition. Non-intrusive emission spectroscopy techniques for the analysis of the plasma (excited species and gas temperature) together with mass spectrometry technique for the identification of gaseous products were successfully applied for understanding by-products formation.

2. Materials and methods

The experimental setup (see Fig. 1) was the same described in [35]. The plasma was created by using a TIAGO device [36] which has been theoretically and experimentally described in [36–38]. The discharge was generated at the end of the tip of a cylindrical hollow metallic rod. The plasma is a jet consisting of a mixing layer around a conical core. In the mixing layers, the plasma gas and the air surrounding the discharge interact. This interaction highly affects the discharge kinetics and equilibrium properties in Ar plasmas [37,38] but also the decomposition routes of ethanol [35].

In the current research, high-purity Ar (99.999%) gas was used to initiate and feed the discharge with flows ranging from 0.15 to 1.50 L/min controlled by a HI-TEC controller (HI-TEC, Bronkhorst). After ignition, ethanol (EtOH) was added to the discharge in gas phase after being evaporated by means of a gas-phase liquid delivery system (CEM, Bronkhorst) with quantities ranging from 0.22 to 1.00 g/h. A constant input power (300 W) was supplied in a continuous mode by a 2.45 GHz SAIREM microwave generator (GMP KG/D) equipped with a water cooled circulator to avoid power reflection damage.

As it has been previously indicated, the goal of this research is to find and understand plasma processes which promote the formation of gaseous and solid products at the plasma exit through different ethanol decomposition routes. For that reason, Optical Emission Spectroscopy (OES) and Mass Spectrometry (MS) have been used as analysis-techniques. On the one hand, to infer plasma kinetics and the formation of plasma species, plasma radiation was directed to the entrance slit of a 1-m focal length Jobin-Yvon-Horiba monochromator (1000 M. Czerny-Turner type) equipped with a holographic diffraction grating of 2400 grooves/mm. Besides, a Symphony CCD (CCD-1024x256-OPEN-STE) was used as radiation detector. On the other hand, a quadrupole mass spectrometer (QMS, PT M63 1121, mod. Omnistar, Pfeiffer Vacuum Technology) was utilized to analyse the composition of the gas exiting the discharge, as well as to quantify hydrogen production thanks to a previous calibration. In order to prevent solid by-products from entering into this device, a filter (re. 33127-201 Iberfluid, Spain) was placed between the reactor and the spectrometer probe.