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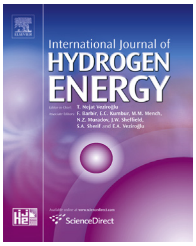

Ethanol reforming into hydrogen-rich gas applying microwave ‘tornado’-type plasma

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Ethanol reforming in microwave argon plasma, operating at 2.45 GHz under atmospheric pressure and vortex gas flow has been investigated. Hydrogen, carbon monoxide and solid carbon are the main outlet products. H_2 and CO have been detected by mass spectrometry (MS) and Fourier transform infrared spectroscopy (FT-IR) whereas “black” carbon deposited at the wall has also been observed. The hydrogen yield has an average value of 98.4%, for ethanol fluxes in the range 4–15 sccm. An increase of about 32% in the energetic hydrogen mass yield has been observed as compared to laminar flow conditions.

A theoretical model based on a set of non-linearly coupled differential equations accounting for the gas thermal balance and the chemical kinetics has been developed. An integral reaction scheme considering ethanol decomposition via two parallel channels was proposed and experimentally validated. Taking into account the diffusion of carbon into colder zones, the formation of solid carbon has also been analyzed. Some part of the solid carbon is deposited on the tube wall while another part is carried away with the outlet gas flow. The theoretical predictions for the H_2 and CO relative densities agree well with experimental data.

1. Introduction

Ethanol is a renewable energy source with a great potential in fuel cell application. It is produced mostly from renewable biomass such as corn (in USA) and sugarcane (in Brazil), and also from any type of biomass and agricultural waste [1]. The conversion process of biomass involves fermentation of the biomass sugars to ethanol. The utilization of ethanol is widespread as a transportation fuel – individually and as a supplement to gasoline (E85), thus reducing both the dependence on oil fuels and the greenhouse gas emission. From the economic perspective, the use of ethanol is very attractive since the biomass feedstock is available in abundance and can be considered as a sustainable resource supply. A great benefit is also the disposal of solid agricultural wastes [2,3]. In recent years, ethanol has been regarded as an effective hydrogen storage, which is safer, cheaper, and more easily transported than hydrogen gas. The interest in hydrogen producing technologies has increased significantly with the implementation of fuel cells – electric power sources with high efficiency and low level of pollutant emissions. Also, hydrogen has the highest heating value as compared with other fuels – the heat released during hydrogen combustion is 142 kJ/g, while it is only 29.7 kJ/g in the case of ethanol [4].

Among the existing conversion technologies of hydrocarbons into hydrogen-rich gas such as partial oxidation, steam

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reforming, and pyrolysis [5], plasma-assisted reforming is already acknowledged as a promising alternative method [6–8]. Plasmas serve as a thermo-chemical device that creates radicals in addition to free electrons, and maintains high gas temperature. The ability of thermal and various types of nonthermal plasmas to decompose different hydrocarbons have been studied elsewhere [5–20]. The conversion of alcohols into hydrogen by dielectric barrier discharge [21,22], gliding arc discharge [23], corona discharge [24], pulsed discharge [25,26], microwave discharge [27–30], glow discharge [31] and others [32–34] has been investigated. Thermal plasma systems have shown a lack of chemical selectivity, too high temperature and power consumption. On the contrary, nonthermal plasmas have the advantage of high selectivity and energy efficiency of plasma chemical reactions, along with effective operation at lower temperatures [19,20].

Microwave-generated plasmas possess some specific features and advantages as compared to other nonthermal plasmas [35,36] as they provide a non-equilibrium plasma with high electron temperature and relatively low (2000–5000 K) gas temperature. Moreover, microwave plasmas can be produced in simple reaction vessels with no electrodes. The absence of electrodes prevents problems such as electrode erosion, discharge pollution, and additional energy consumption for cooling. Practical advantages of microwave plasmas include also the following: absence of high DC voltages; availability of inexpensive microwave sources at 2.45 GHz; flexibility of operation conditions at different pressures and with different background gases. Of particular importance is that the microwave power is very efficiently absorbed by the plasma, which provides high concentrations of energetic electrons and free radicals in the discharge. These properties make them suitable environments to dissociate complex molecules. Several authors have investigated microwave plasmas for reforming of methane [37–41]. Effective reforming of kerosene and methane using air microwave discharge at atmospheric pressure was reported in [42]. Steam reforming of n-hexane and isooctane has been performed in [43,44], although with insufficient conversion.

Low-pressure surface-wave discharges have been employed to decompose ethanol in [29]. The same type of microwave discharges but at atmospheric pressure have been used to study the conversion of various alcohols [27], for reforming of methanol [30], as well as for reforming of three different alkanes [45]. Our previous work has also shown promising experimental results for reforming of methanol and ethanol, under Ar and Ar-water laminar flow conditions [28]. Introducing a small quantity of water vapor results in a nearly double increase of hydrogen production rate [28]. However, using purely steam plasmas implies some experimental difficulties associated with discharge stable operations, higher feeding power, additional heating of delivering pipes as well as low conversion rates. The advantages of vortex gas flow compared to laminar flow along with detailed kinetic modeling of the methanol decomposition process were presented in a previous work [46]. High conversion rates (~100%) achieved using microwave plasmas as a tool for alcohols reforming should be pointed out [27,28,46].

In the present study, a surface-wave driven microwave 'tornado'-type plasma at atmospheric pressure conditions has been used for ethanol conversion into hydrogen-rich gas. A surface-wave sustained plasma is a special type of microwave plasma, where the microwave power is transferred to the plasma by the electric field of a guided wave. The plasma is created and maintained under vortex flow conditions using mixtures of pure Ar with ethanol vapor. In order to create a stable discharge with effective cooling a swirl system has been used. Optical Emission Spectroscopy (OES) has been applied to detect the emission of radiative species created in the plasma and to determine the main plasma parameters. The products from the plasma decomposition in the outlet gas stream were characterized by Mass Spectrometry and Fourier Transform Infrared Spectroscopy.

A kinetic model describing the ethanol decomposition in the argon plasma environment was also developed. The calculations have been performed considering either homogeneous, *i.e.*, only gas phase, or heterogeneous (gas phase + solid carbon) environments. The diffusion of gas-phase carbon has been estimated from detailed analysis of the experimental data. The theoretical predictions for the H_2 and CO relative densities agree well with experimental data.

2. Experimental setup and conditions

The scheme of the experimental setup is shown in Fig. 1. A generator (Sairem) provides the microwaves at 2.45 GHz and maximum power of 2 kW. The microwaves travel through a waveguide system (WR-340), which includes a water-cooled circulator, directional couplers, a 3-stub tuner, a moveable short-circuit and a waveguide surfatron as a field applicator [47]. The moveable short-circuit together with the 3-stub tuners allow for impedance matching so that maximum electric field is achieved at the launcher position. The discharge ignites in a quartz tube (1.5 cm inner and 1.8 cm outer diameters, respectively), placed vertically and perpendicularly to the waveguide wider wall. In this work, the microwave power was kept at 450 W and the total Ar flow (Q_{Ar}^{tot}) at 1000 sccm. The ethanol flow rate was determined by calibration.

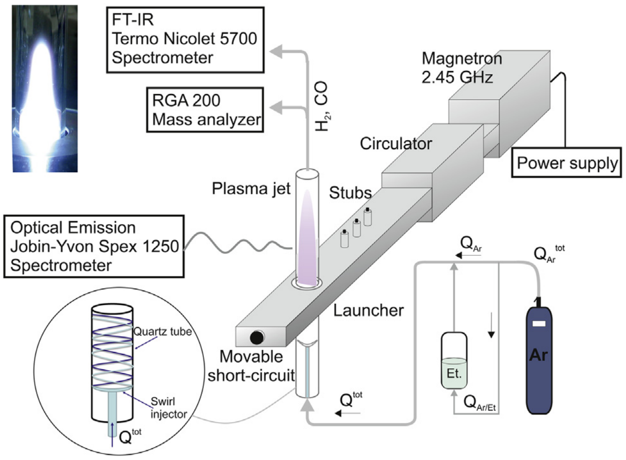

Fig. 1 – Scheme of the experimental setup, sketch of the swirl system and a picture of the argon/ethanol plasma torch.