Methane and Ethane Decomposition in an Atmospheric-Pressure Plasma Jet

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Abstract—This paper reports on studies obtained from RF-driven atmospheric-pressure plasma-jet excitation of methane and ethane. Differentiation with other works is achieved in that others have considered hydrocarbon decomposition at either low pressure or high temperature. In our experiments, we can clarify the effect of pure-plasma treatment of hydrocarbons, as opposed to the thermal effect of gas heating that results in pyrolysis. Gas-chromatography analysis was used to detect and quantify the main decomposition products. Kinetic modeling of the pertinent chemistry was performed by dividing the reactive system in two main parts: a plasma region where the electron impact processes leading to decomposition are considered and a postplasma region where recombination of nonstable species occurs. A reasonable qualitative agreement between the experimentally measured by-product concentrations and the calculations was achieved. It is observed that our proposed recombination mechanism correctly predicts ethane and ethylene formation from a CH₄ discharge and methane, ethylene, propane, and acetylene formation from the C₂H₆ discharge. By means of calculations, the main role of radicals in the pertinent hydrocarbon chemistry under nonthermal plasma conditions is confirmed.

Index Terms—Atmospheric-pressure plasma jet (APPJ), electron-impact process, plasma-assisted combustion, recombination model.

I. INTRODUCTION

Interest in nonthermal plasmas as a tool to alter combustion properties of hydrocarbons has increased in the last several years. Some nonthermal-plasma technologies have been developed to pretreat fuels just prior to combustion. A nonthermal plasma signifies less waste of energy in terms of heat or high temperature. In our experiments, we can clarify the effect of pure-plasma treatment of hydrocarbons, as opposed to the thermal effect of gas heating that results in pyrolysis. Gas-chromatography analysis was used to detect and quantify the main decomposition products. Kinetic modeling of the pertinent chemistry was performed by dividing the reactive system in two main parts: a plasma region where the electron impact processes leading to decomposition are considered and a postplasma region where recombination of nonstable species occurs. A reasonable qualitative agreement between the experimentally measured by-product concentrations and the calculations was achieved. It is observed that our proposed recombination mechanism correctly predicts ethane and ethylene formation from a CH₄ discharge and methane, ethylene, propane, and acetylene formation from the C₂H₆ discharge. By means of calculations, the main role of radicals in the pertinent hydrocarbon chemistry under nonthermal plasma conditions is confirmed.

Some works in the field of plasma-assisted combustion have been carried out using a dielectric-barrier-discharge reactor to activate pure hydrocarbons and hydrocarbon/air mixtures with very promising results [2], [3]. But it is of paramount importance to better understand the chemical-activation mechanisms involved in these novel techniques to achieve practical applications.

In the past several years at the Los Alamos National Laboratory, a new nonthermal plasma source called the atmospheric-pressure plasma jet (APPJ), was developed as a system for a number of applications, such as materials processing and surface decontamination [4], [5]. The APPJ discharge is essentially different from other atmospheric-pressure plasma sources, because it is characterized by a stable, volumetric, and homogeneous discharge, which fills the volume between the electrodes [6]—attributes that make it a potential technique to study and model the basic nonthermal plasma triggered hydrocarbon chemistry.

Some of the characteristics of the APPJ have been already studied [5]. It produces a homogeneous discharge at atmospheric pressure using 13.56-MHz RF power, utilizing a predominate fraction of helium feed gas to stabilize the discharge, and consequently, it is characterized by a relatively low breakdown field of ~1 kV/cm. The APPJ operates without any dielectric-electrode cover yet is free of filaments, streamers, and arcing. The gas temperature of the discharge is typically between 50 °C and 300 °C, so thermal effects on hydrocarbons can be easily separated from the study of electron-driven processes [4].

While passing through the APPJ, the feed gas becomes excited, dissociated, or ionized by electron impact, producing an effluent stream of highly reactive chemical species. In this paper, the reaction-species production is estimated by means of the ELENDIF code [7], which is capable of calculating the electron-energy distribution function and convolving it with the cross sections of different electron-impact processes, giving, as a result, parameters such as the electron drift velocity and specific electron-impact rate coefficients that can be used to estimate the decomposition product concentrations per deposited plasma-energy density, expressed as a G-value (i.e., product yield in molecules per 100-eV deposited energy). For example, for the following reaction:

\[ e + AB \xrightarrow{k_1} A + B + e \]

\( k_1 \) represents the specific rate coefficient for the stated process. Now, the G-value can be defined for each different product of the reaction

\[ G_A = \frac{n_A}{\varepsilon_d} = \frac{k_1}{q} \int_0^t \frac{n_e n_{AB} dt}{\int_0^t n_e v_d E dt} = k_1 \frac{n_{AB}}{qv_d E} \]

where \( n_A \) is the concentration of the A species, \( \varepsilon_d \) is the plasma energy density, \( q \) is the charge on an electron, \( n_e \) is the electron concentration, \( v_d \) is the electron drift velocity, and \( E \) is the electric field.

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