H_2 temperature measurements in a CH_4 microwave plasma for the production of higher hydrocarbons

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Abstract: In this contribution, we report molecular hydrogen temperature measurements in a microwave-driven methane plasma by Raman scattering. Laser Induced Fluorescence on C_2 overlaps the H_2 Raman scattering spectrum, which was partially circumvented using the polarization of the scattered Raman signal. The impact of the hydrogen admixture on the temperature, conversion, and the product distribution will be presented.

1. Introduction

Methane (CH_4) is an unavoidable side product of the cracking of naphtha. It is highly desirable to convert this molecule to higher hydrocarbons such as ethylene (C_2H_4) and acetylene (C_2H_2), which are precursors for further chemical processes. Methane conversion to higher hydrocarbons in a plasma reactor is an attractive route since it can be switched at short timescales and powered by green electricity, reducing the carbon footprint[1]. The product distribution of such a reactor is the result of the kinetics, which is governed by the temperature.

Raman scattering is a non-intrusive temperature diagnostic. In methane plasmas, this scattering scheme is complicated by the fluorescence of C_2 radicals, which is excited by the 532 nm laser light. In this contribution, we present temperature measurements by Raman scattering in a microwave reactor and the resulting product distribution under conditions with low C_2 densities.

2. Methods

Mixed hydrogen/methane discharges are generated in a 26 mm diameter quartz tube by 2.45 GHz microwaves. The plasma is stabilized by the gas flow via swirl injection. The product composition is analyzed with gas chromatography. A vertically polarized 532 nm Nd:YAG laser shoots axially through the reactor. Scattered light is collected perpendicular to the laser path. Rayleigh scattered light and straylight are blocked by a long-pass filter. Light is collected for both polarization directions separately to reduce the LIF signal (which is unpolarized) with respect to the H_2 Raman signal (which is mostly polarized). The scattered light is transmitted through an optical fiber bundle to the Andor, ENI-01313 Kymera 328i spectrometer, which is equipped with an ICCD camera. The H_2 Raman spectrum is measured in the 3700-4200 cm^{-1} range which is relatively undisturbed by C_2 fluorescence. The spectrum is fitted under the assumption that the vibrational temperature is equal to the rotational temperature.

3. Results and Discussion

The plasma reactor was operated at 50 mbar to reduce C_2 fluorescence in the Raman spectrum. A scan of input power was made at three different (H_2, CH_4) flow combinations: (12 slm, 8 slm), (10 slm, 10 slm), and (8 slm, 12 slm). Measured temperatures are in the range of 2000 K to 2500 K as shown in Figure 1. The temperature increases with power and with increasing hydrogen admixture. For an equal hydrogen/methane mixture in thermal equilibrium at 50 mbar, the temperature range between of 1500 K and 2700 K is optimal for acetylene production with full conversion and other products below 1 %. In the reactor the temperature profile has a radial dependence, which combined with the flow dynamics and chemical kinetics determines the conversion. A CH_4 conversion of up to 30 % was observed in the three mixing scenarios, i.e. more methane conversion in absolute terms at higher methane flows. The selectivity towards acetylene varied between 60 % at 500 W and 80 % at 1.1 kW. Ethylene and ethane are the remaining products; the ethylene to ethane proportion increased from 2-1 at 500 W to 3-1 at 1.1 kW.

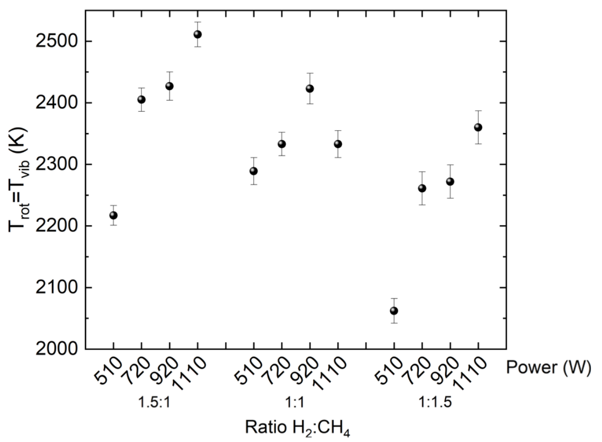

Fig. 1. H_2 rovibrational temperatures in microwave-driven mixed hydrogen/methane plasma at 50 mbar

4. Conclusion

Temperatures in mixed H_2/CH_4 plasmas are determined with Raman scattering on H_2. Special measures were needed to minimize the impact of C_2 fluorescence on the measured spectra. It is foreseen to improve the diagnostic technique so that temperatures can be measured at parameters which show a higher conversion.

References

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