Diagnostic characterisation and 0D modelling study of ns-pulsed plasma-assisted methane pyrolysis

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Methane (CH_4) is the second largest contributor to global warming [1] and consequently, there is a growing focus on converting CH_4 into value-added products. CH_4 conveniently contains four hydrogen atoms which can be used to synthesise hydrogen gas (H_2), offering a viable alternative for storing energy in a chemical form. This strategy enables the retention of the energy surplus generated during peak production hours (in the form of H_2) and later employment for eventual energy deficits, thus addressing issues related to the intermittent nature of renewable energy sources.[2] Additionally, H_2 stands out as a valuable energy source because it can supply more energy per kilogram than fossil fuels, facilitating the reduction of fossil fuel exploration and resultant greenhouse gas emissions.[3]

Plasma-assisted methane pyrolysis for H_2 production combines the advantages of fast and cost-effective gas heating, along with CH_4 dissociation occurring at lower gas temperatures (induced by electron impact reactions) than those required for thermal pyrolysis. Also, it boasts low energy input demand and complete CO_2 neutrality, addressing major drawbacks of competing technologies (steam methane reforming and water electrolysis).[4,5] Nanosecond pulsed plasmas enable the generation of high electron densities and a strong non-equilibrium medium that stimulates CH_4 conversion under relatively mild conditions, typically resulting in a high energy efficiency.[6] Nonetheless, chemical and physical fundamental knowledge regarding CH_4 pyrolysis in these types of plasmas remains scattered, which limits the industrial uptake of the process. Thus, this work aims to bridge this knowledge gap in the plasma field and investigate various properties of nanosecond pulsed plasmas via a combination of both plasma diagnostics and 0D modelling techniques.

The experimental investigation was conducted in a pin-to-pin plasma reactor in a CH_4 atmosphere within a pressure range of 0.5 to 2.0 bar. Specifically, we performed electrical characterisation of the discharges, spectroscopic measurements of plasma volume, electron density, kinetics of gas heating and ground state species formation, while examining the effect of the applied pressure. For this purpose, time-resolved ICCD imaging, optical emission (OES), Rayleigh scattering, and laser-induced fluorescence (LIF) spectroscopies were employed. As displayed in Table 1, an increase in pressure causes a decrease in the peak electrical power and plasma volume. This decrease can be attributed to the higher gas density at elevated pressures, resulting in a lower specific energy input per CH_4 molecule, subsequently leading to lower peak electron density and gas temperature.

Table 1: Key experimental parameters measured at different applied pressures.

Pressure (bar)	Peak power (MW)	Plasma volume (mm^3)	Peak electron density (10^{17} cm^{-3})	Peak gas temperature (K)
0.5	7.6 ± 0.7	1.0 ± 0.1	8.72 ± 0.02	2868 ± 221
1.0	6.9 ± 0.3	0.8 ± 0.1	4.59 ± 0.01	1842 ± 172
1.5	5.3 ± 0.5	0.8 ± 0.1	2.10 ± 0.01	1410 ± 138
2.0	4.7 ± 0.2	0.7 ± 0.1	1.14 ± 0.01	920 ± 96

Furthermore, temporal gas temperature profiles have been compiled from three complementary spectroscopic techniques (OES of CH(X), OES of C_2 Swan and Rayleigh scattering, see Figure 1). These have revealed that the peak gas temperature is reached 1 µs after applying the pulse and sustained for ca. 4 µs. Subsequentely, the cooling process commences and lasts for ca. 30 µs (not shown in Figure 2), showing effective gas heating during the ns-pulsed plasma event.

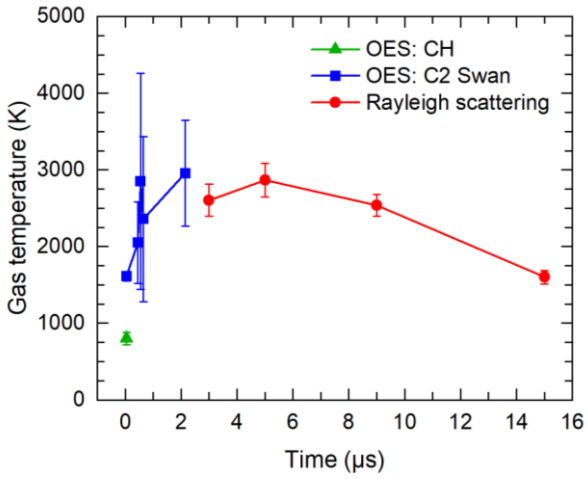

Figure 1: Gas temperature as a function of time measured by three techniques (OES of CH(X), OES of C_2 Swan band and Rayleigh scattering) at an applied pressure of 0.5 bar.

To reveal the plasma chemistry initiated in such pulsed plasma conditions, a 0D model (ZDPlasKin in tandem with Bolsig+) was developed with the goal of describing the chemical pathways that drive CH_4 plasma pyrolysis. The model comprises 81 species and 4483 reactions (ground-state, vibrationally and electronically excited molecules, radicals, ions and electrons). The electrical power was emulated by triangular pulses and experimentally proven gas temperature profiles were implemented in the simulations. While H_2 remains the main product, the model shows a correlation between rising pressures and reduced CH_4 conversions, alongside a shift in C_2 product selectivity from C_2H_2 (at lower pressure) to C_2H_6 (at higher pressure). Model validation was performed by comparison with experimentally recorded electron, CH(X), and H radical densities and kinetics.

This comprehensive approach, which integrates both modelling and experimental endeavours, converges towards important conclusions regarding the effect of pressure and gas temperature on CH_4 conversion and product selectivity, analysis of reaction pathways, and evaluation of the importance of electronic and vibrational excitation in the overall H_2 formation mechanisms.

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