Investigation of soot inception in methane plasma-pyrolysis by laser diagnostics

D.C.M. van den Bekerom[1], S. Mirpour[1], Y. Creyghton[1], D. Del Cont-Bernard[2], T.W.H. Righart[2], J.L. Linden[1], G.J. van Rooij[2], T. Butterworth[2]

[1] *Netherlands organisation for applied scientific research TNO*
[2] *Departement of Circular Energy and Engineering, University of Maastricht*

Abstract: Plasma conversion is under investigation for use in non-oxidative methane coupling to produce value added hydrocarbons. At the Brightsite Plasmalab, plasma pyrolysis is used to produce acetylene, ethylene, and hydrogen. Soot formation is a competing process that provides a sink for carbon atoms, deteriorating hydrocarbon selectivity. Laser Induced Incandescence (LII), a spatially and temporally resolved laser diagnostic that can detect soot particles, is developed to monitor the inception of soot in a microwave discharge.

Keywords: non-oxidative coupling of methane, Laser Induced Incandescence, soot formation

1. General

The chemical industry must radically innovate to replace fossil fueled chemical processes in an effort to reduce CO_2 emissions. Electrification is an important step in reducing the CO_2 footprint of chemical plants. In the case of Naptha crackers, one of the main pollution sources, electrification of the plant leaves unused methane that used to be burned in the process. This methane can be valorized by converting it to a value added product. Plasma pyrolysis is under consideration to electrically convert methane into ethylene for this reason.

The Brightsite plasmalab, a consortium of TNO, University of Maastricht, Sitech, and Brightlands campus, was established to study the economical feasibility of plasma conversion processes and importantly, investigate the challenges of scaling up the technology. To do this the Brightsite consortium works on three generations concurrently; Generation 1 aims at replicating the industrially established Huels process on a pilot plant scale (500kW), where methane is converted to acetylene at high conversion rates. Generation 2 aims at developing an optimized Huels process, still producing acetylene, but with optimized flow patterns, temperature profiles and reactor geometries. In Generation 3, the feasibility of direct formation of ethylene is investigated.

The pyrolysis of methane can produce ethylene or acetylene by following the Kassel-mechanism [1]. Here, methane is first dehydrogenated to methyl radicals at high temperature. The methyl couples to ethane, which then follows stepwise dehydrogenation to ethylene and acetylene. Once acetylene is present in significant quantities, it can polymerize to Polycyclic Aromatic Hydrocarbons (PAH), which are well known to be precursors for soot. The key to high selectivities in plasma pyrolysis is therefore to decrease residence times to limit soot formation and quench the reaction kinetics once a sufficient fraction of ethylene or acetylene is reached. The presence of soot, and more precisely its inception, is thus a key indicator of degraded C_2H_x yields. By monitoring the absolute fraction of soot in the plasma, conditions for optimal conversion could be retrieved.

Soot has been studied for many decades in the combustion community for its role as pollutants in engine exhausts, where it has been linked to a number of adverse environmental and health effects. Laser Induced Incandescence (LII), a laser diagnostic allowing quantitative detection of soot, is a well-established diagnostic with a relatively simple setup, yet spatially and temporally resolved detection capability [2]. LII relies on the soot particles' strong absorption, resulting in most of the incident laser energy to be absorbed. The absorbed energy causes the particle to rapidly heat up to temperatures above 3000K, at which point broadband black body radiation is emitted in the visible, which can be detected by a dispersive imaging system such as a spectrometer with an intensified camera.

2. Optical Layout

The optical layout is shown in figure 1 and consists of a pulsed Nd:YAG laser, operated at either the fundamental 1064 nm, or second harmonic at 532 nm. The laser produces pulses of up to 1J at 532 nm at 30 Hz, with a nominal pulse width of 6 ns. The laser is focussed into the radial centre of a 26 mm ID quartz tube containing the plasma. The quartz tube intersects with a microwave applicator where the microwaves are launched into the

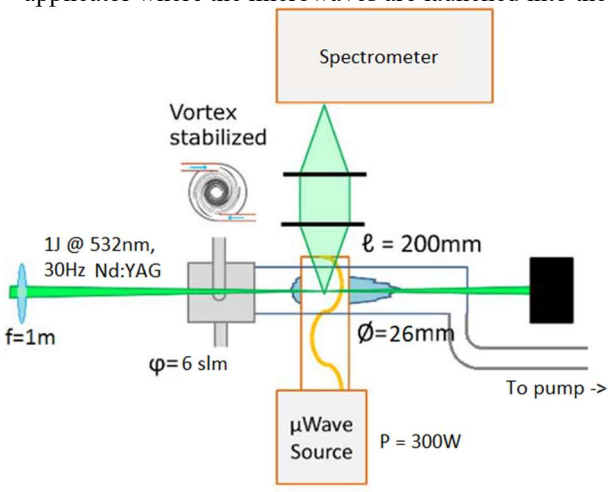

Fig. 1. Optical layout of the laser system. Signatures of LII and vibrational Raman scattering can be recorded simultaneously.

plasma. A tangential flow provides vortex stabilization to the plasma. The incandescence signal is recorded perpendicular to the laser beam at two separate axial locations: in the plasma centre, where optical access is provided through a hole in the microwave plunger, and in the afterglow, downstream of the plasma where optical access is unrestricted. The captured light is collimated, passed through a notch filter to block the laser wavelength, and focussed on a fiber array that is imaged onto a 300 l.mm^{-1} grating in a 25 cm Czerny-Turner spectrometer, capturing a range of 400 nm – 650 nm. The dispersed light is imaged in 1D along the axial direction, capturing an axial extent of ~2 cm. While the high intensity laser pulse interacting with the soot particles is technically not non-intrusive, the pulse width is likely too short (6 ns) to have a significant effect on chemistry. In addition to the laser diagnostics, a commercial camera records color images of the plasma optical emission for reference.

When operated at 532 nm, a number of laser induced process will interfere that complicate interpretation of the measured spectra. Vibrational Raman, which is a laser scattering process, is near-instantaneous and does not extend beyond the laser pulse duration. Moreover, the spectral distribution is limited to a few isolated bands, making it relatively simple to separate from LII by recording the signal at wavelengths without Raman signature. Because the two can be isolated in this way, the Raman signal can be used to measure the temperature, as was done in a similar setup in earlier work [3]. The LII signal duration depends on the laser fluence. At high fluence it is as short as a few ns, while at lower fluence it can be as long as a few 100 ns. By choosing a fluence where the signal survives beyond Raman scattering, separation of the two signals is further facilitated. In addition there is Laser Induced Fluorescence (LIF) by CH and C_2 species. Under the studied conditions, the LIF signal by C_2 is most significant. Due to the fact that the emission is fairly broad and covers most of the spectral range used for detection [4], it is separated from LII based on its comparatively long time constant of ~100 ns. The camera gate delay with respect to the laser was scanned over a range from 0 to 200 ns. The spectrum at later time delays was fitted with an exponential time decay, which was extrapolated to the earlier time delays to remove the contribution by C_2 LIF. After removing these two interfering contributions, the remainder is mostly LII signal. A simpler way to record interference-free LII signals is by irradiating the soot particles by 1064 nm laser pulses, which would eliminate LIF and Raman scattering in the visible range. The downside of this is that Raman scattering cannot be used for concurrent temperature measurements.

3. Absolute volume fractions

The LII signal consists entirely of thermal radiation from the laser-heated soot particles. The spectral radiance of the recorded signal is therefore a known function of particle size (i.e. a Planck curve). By absolutely calibrating the spectrometer spectral sensitivity, absolute volume fractions can be obtained from the LII signal. First the spectrometer's spectral response was determined by measuring the spectrum of a known light source (SLS201L) and dividing the measured spectrum by a pre-recorded reference spectrum of the calibration lamp. After correcting for the spectral response, spectra of a tungsten filament lamp at a number of different currents were recorded. After correcting for the emissivity of tungsten, these spectra were fitted with a Planck curve to obtain the filament temperature at different currents, shown in figure 2. By taking the surface area of the filament and solid angle of the collection optics into account, the sensitivity of the camera is calibrated absolutely in Watts per count. The absolute radiance in W.sr^{-1}.nm^{-1} can then be directly inferred from the measured LII spectra, which can be directly related to the volume fraction of soot particles f_v [5]:

$$f_v = A \frac{V_{exp}}{\frac{E_m(\lambda)}{\lambda^6}\left[\mathrm{e}^{\frac{hc}{kT\lambda}}-1\right]^{-1}}, \quad (1)$$

where V_{exp} is the experimentally measured signal, A the calibration factor determined through calibration with the filament lamp, $E_m(\lambda)$ the wavelength dependent emissivity of the soot particle, h the Planck constant, c the speed of light in vacuum, k is Boltzmann's constant, λ the wavelength, and T the temperature.

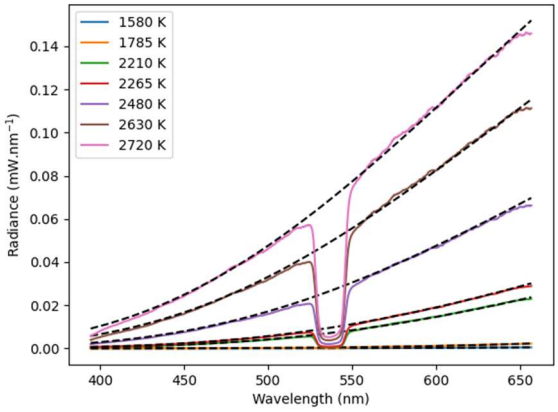

Fig. 2. Fit of filament lamp radiance used for absolute calibration of the spectrometer. The notch filter blocks wavelengths in the range of 530-540 nm, which is not included in the fit.

4. LII measurements in the plasma afterglow

LII spectra were recorded in the plasma afterglow directly after the waveguide, at pressures of 25, 30, and 35 mbar. The pressures were chosen because they are at the onset of soot formation, indicated by an orange glow in the plasma which is clearly present at 35 mbar but not at 25

mbar. Figure 3 depicts the spectra measured at these pressures, with gate delays of 0, 20, and 40 ns. As discussed earlier, Rayleigh and Raman peaks are visible (green and orange shade respectively), but disappear when the gate delay is increased. Interference by C_2-LIF is substantial, and only a few bands lack C_2-LIF features and can thus be used for inference of incandescence intensity and particle temperature, indicated in blue in figure 3.

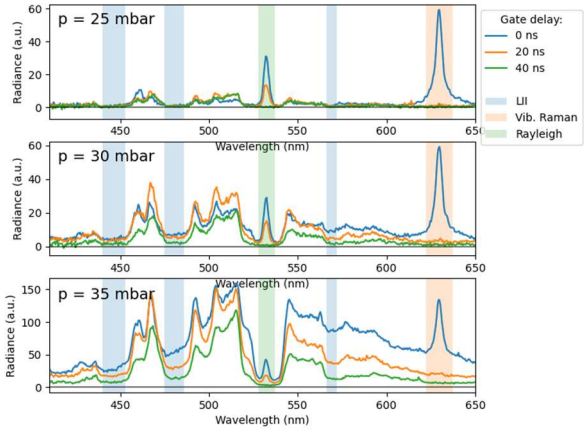

Fig. 3. LII measurements at three different pressures near soot inception, recorded at different gate delays. Interfering bands from Rayleig, Vib. Raman, and C_2 LIF are clearly present. The blue bands indicate pure LII signal.

As the pressure is increased above the pressure at which the orange glow is first visible, both the LII signal as well as the C_2-LIF signals significantly increase in intensity. The increase in carbon formation at higher pressures can be attributed to either increased residence time because of lower flow velocities, or increased kinetics due to an increase in temperature. Measuring the temperature from Raman scattering will shed more light on the precise mechanism in the near future. In the measurements at a laser wavelength of 532 nm undertaken thus far, the C_2-LIF interference is so overwhelming that reliable fitting of the LII signal is prohibited. To solve this problem, LII signals at a laser wavelength of 1064 nm will be recorded next, where such an interference should be minimal.

5. Conclusions

A plasma process for the conversion of methane to olefins is under development. In order to selectively produce the desired products, ethylene and acetylene, fast quenching that freezes kinetics is needed to prevent conversion to C(s), resulting in soot formation. A Laser Induced Incandescence diagnostic was developed to study the formation of soot in the plasma. A strong increase in both C_2-LIF and LII signal is observed at the onset pressure of soot formation. At the current laser wavelength C_2-LIF dominates the spectrum, which will be circumvented by employing a laser wavelength of 1064 nm.

6. References

[1] J. R. Fincke et al., INEL Report (2000)
[2] Michelsen et al., Prog. Energ. Comb. Sci. **51** (2015) 2–48
[3] Butterworth et al., J. Quant. Spectrosc. Rad. Transfer
[4] Carbone et al., Plasma Sources Sci. Technol. **29** (2020) 055003
[5] Snelling et al., Applied Optics, **44** (2005) 31
236 (2019) 106562