How is soot formed in combustion processes?

C.J.M. Hessels, R. Doddema, N.G. Deen, N.J. Dam
Multiphase and Reactive Flows group, TU Eindhoven

Knowledge is a prerequisite for innovation. For complex processes, like the formation of soot in hydrocarbon fuel combustion, highly detailed optical measurements elucidate details of the underlying process, and provide a benchmark to calibrate numerical models.

The delightful stench of burnt meat from your neighbours’ BBQ, the impenetrable black of the exhaust plume of an oldtimer pick-up truck, the warm orange glow of a camp fire. All are manifestations of a ubiquitous yet poorly understood process associated with the combustion of organic fuel, namely soot formation. The problem is one of complexity. ‘Combustion’ is a one-word container for a chemical soup, a blizzard of zillions of molecules of hundreds of chemical compounds flying around at the speed of sound, colliding and transforming as they go. Ideally, from the clean-combustion point of view, all fuel you feed into a flame should burn to completeness and exit as CO2 and H2O: full conversion, 100% efficiency. Soot formation, from this point of view, is an undesirable side track, a loss channel for carbon that may escape combustion when it makes it into the exhaust. Little is known, on a fundamental level, of the incipient stages of soot formation, the ‘birth of soot’. What would be the smallest ‘soot molecule’? How is that formed out of the initial fuel? And how does it grow? Are there bottlenecks in the process? Detailed measurements might provide some of the answers, but doing reliable and quantitative measurements on individual chemical species in the hostile environment of a flame is a challenge in itself.

What are the requirements that a suitable measurement technique should fulfil? To answer this question for this particular case, let us travel. Let us join a small fuel pocket on its way through a flame, like that of Figure 1. The particular flame under study is a stationary, non-premixed flame: pure fuel exits a stainless steel nozzle and flows into ambient air. Initially, oxygen is present only at the periphery, and there is no oxygen in the core of the fuel flow. Thus, our travel companion, the fuel pocket, grows hotter and hotter while it flows along, approaching the actual flame location, but it cannot burn because there is no oxygen. Due to the increasing temperature, however, the fuel molecules decompose anyway (pyrolysis), new carbon-rich compounds form and from these precursors soot is born, it grows, and eventually most of it burns anyway in regions where sufficient oxygen has diffused into the flame.

Our measurement technique should be able to resolve these processes in space, be able to distinguish individual chemical compounds, and to do so without affecting the flame at all. There is a particular type of optical measurement technique that admirably fulfils all these criteria, viz. Raman spectroscopy. The principle behind this technique is as follows.
When a gas (mixture) is illuminated with a beam of monochromatic light, part of the light is scattered out of the beam; not much, but easily detectable with modern equipment. Most of this scattered light has the same wavelength (colour) as the incident light (Rayleigh scattering), but a tiny fraction (about 0.1%) has acquired a different wavelength (Raman scattering). This wavelength change (called the Raman shift) is the net result of an intricate interaction between the electronic charge distribution that is set into oscillation by the incident light (an electromagnetic wave itself) and the natural vibration of the nuclear framework of the scattering molecules. The former is governed solely by the incident light, but the latter largely depends on the properties of the molecules. Strong chemical bonds are associated with high-frequency vibrations of small amplitude, whereas weak bonds lead to slow vibrations of large amplitude. Thus, the colour change, the Raman shift, is highly specific for the individual chemical species which are responsible for the scattering.

In our experiments the flame is illuminated along its central axis by a thin line of perfectly green laser light (527 nm sharp). Scattered light is collected by a so-called imaging spectrograph, a device that splits the collected light into its constituent colour components, and does so for all locations along the laser beam simultaneously. Its output is recorded by a CCD camera equipped with an image intensifier, all in all resulting in a device with nearly single photon counting capabilities. Photographs recorded by the CCD camera thus contain spectral information (the colours in the Raman-scattered light) along the horizontal direction, and spatial information (along the central axis of the flame) along the vertical direction. An example, recorded on a simple natural gas flame, is shown in Figure 2. This ‘photograph’ is presented in false-colour format, that is, the intensity of the scattered light falling on each individual pixel (that is, each wavelength/location-combination) is translated into a particular colour in the picture.

As expected, the spectra are dominated by contributions of the most prevalent compounds in the flame: fuel, nitrogen, water vapour, and the like. These give rise to detailed features at highly specific wavelengths, as indicated in the figure. There is also soot: the fat band spanning all colours. By combining spectroscopic information from literature, we were able to identify most of the spectral features and to quantitatively simulate the spectra of most major compounds in the flame. Comparison with numerical calculations performed on the same flames has shown good agreement with the experiments for natural gas, the fuel for which the ‘numerical chemistry’ is best developed. As soon as the fuel becomes a little bit more involved (ethylene rather than methane, for instance), the numerical models start to deviate from the experiment, indicating that more work needs to be done on the reaction mechanisms. This exemplifies the benchmark capabilities of our experimental setup. Having established agreement between experiment and numerical simulation in a situation where agreement is to be expected, we can trust the experimental results on more involved cases and use them to calibrate the numerics.

The backbone structure of these flames has thus been characterized in great detail. Now we can start looking for perturbations, small deviations in the spectrum that signal the presence of soot precursors.

The groundwork has been laid, the hunt is on!