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Laboratory : Institut Jean le Rond d'Alembert

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Title of the thesis: Control of the soot history in flames: application to the synthesis of nanostructured materials

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Thesis's summary (abstract):

These PhD works intend to explore the potential of steady smoking flames to be very reproducible generators of particles with characteristics (size, crystallinity, morphology) that could be appropriately controlled.

To this end, the transition from the "closed-tip" flame configuration (i.e. conditions that allow for full soot oxidation) to the "open-tip" one (i.e. conditions that allow for soot release) that a laminar 2D axisymmetric coflow non-premixed flame experiences at the smoke point is first to be better understood. The experimental characterization will be conducted with the help of a sophisticated optical diagnostics, i.e. the Modulated Absorption/Emission technique developed at ∂'Alembert Institute. This technique is expected to deliver fields of soot temperature, volume fraction, and morphological characteristics within the flame. These quantities govern the radiative losses from the flame that can lead to the quenching at the flame tip, therefore the potential soot release to the atmosphere.

The conditions at which the flame tip opens and releases soot, i.e. does not favour soot oxidation, especially depend on the carbonaceous particles load produced in the flame and the temperature field at the flame tip. The oxygen content of the fuel stream has been shown to play a key role in the conditions met at the flame tip. As a result, biofuels, especially

oxygenated additives, will be added to the fuel stream to access a wider range of conditions for soot release. Thus, the fuel stream composition and flow rate, oxidizer stream composition and flow rate, and pressure (1-10 atm) will be varied to assess the range of the soot characteristics that the burner can produce. Over this range, soot deposit sampled at the burner exhaust will be ultimately characterized in terms of size distribution, elemental composition, the content in dislocated graphene layers, the content in ash, and the reactivity of the soot produced.

The formation and growing processes of soot being partially governed by chemical reactions, complementary analysis of 1D flat premixed flames structure are also to be operated. The simple geometrical configuration of such a flame is expected to help get a better knowledge of the hydrocarbon chemistry inside the flame and, because this flames can be easily modeled, to test the ability of the chemical combustion mechanism to accurately reproduce this chemistry.

Since the simulation of the transition at the smoke point of 2D flames is crucial to the control of carbonaceous nanoparticles release process from flames, the experimental database produced will contribute to the validation of the CIAO code developed at RWTH Aachen (Germany) as a tool for the prediction of the soot release.

Subject

Context

Energy production and its impacts are traditionally the focus of combustion science. As a result, strategies aiming at soot emissions suppression, if not, mitigation [1,2] have been especially emphasized for the last two decades. Following these efforts, significant insights into the understanding of soot formation, growth, and oxidation have been achieved, using both advanced experiments [3] and numerical modeling [4-6] that open the way to the optimization of “soot-free” processes. In contrast, steady smoking flames can also be considered as very reproducible generators of carbonaceous nanoparticles with characteristics (size, crystallinity, morphology) that are to be appropriately controlled [7]. Nanotechnology is expected to have major impacts in medicine (e.g. drug delivery), electronics (e.g. nanomagnetic switches), and materials science (e.g. nanofilters). Thus, the manufacturing of nanostructured medium offers opportunities in these emerging fields.

Though the technology of flame aerosol delivery dates back to prehistoric times - smoke was used as an illustration for paintings on cave walls -, its potential to create new nanostructured materials for catalysis, composites, and other applications have been recognized only recently [7,8]. Compared to wet chemistry approaches, aerosol technology is advantageous for the production of commercial quantities of nanoparticles because of its high-throughput production, fast processing time, facilitating process design (manufacturing and collecting), and apparent simplicity. As an illustration, the configuration of the axisymmetric coflow non-premixed burner has been widely employed for commercial production of flame-made nanomaterials [8,9].

Among the challenges associated with the design of such a flame aerosol delivery process, the accurate control of the size, the shape, and the chemical composition of the elementary particles used to assemble the nanostructured material is a major issue. Recently, Abboud et al. [10] showed that the size of soot aggregates released by a steady atmospheric axisymmetric coflow non-premixed flame can be controlled, both in terms of mean and distribution, through the addition to the fuel stream of properly selected oxygenated compounds. However, the oxidative reactivity of soot sampled was found to decrease when increasing a given oxygenated coumpound content. This trend was correlated with lower amorphous carbon concentration in soot sampled. As a result, the authors emphasized the need for further investigations on the conditions met at the flame tip, through which soot is released. Further downstream, soot related processes are frozen, especially due to the dramatic temperature drop experienced [4]. Controlling the characteristics of soot released requires fine understanding of the processes leading to soot release itself.

Originally exploited to quantify the soot production propensity of any fuel [11], the smoke point concept has been deeply explored [12-14], suggesting that an axisymmetric coflow laminar non-premixed flame quenches at its tip due to radiative heat losses at fixed critical conditions in soot concentration and temperature. Flames can be “closed-tip” (below the smoke point) when fuel is consumed before these critical conditions are attained, or “open-tip” (beyond the smoke point) if quenching occurs before the fuel is fully consumed, soot particles being released through the open flame tip.

Soot production is one of the most complex combustion related phenomena since it stands at the heart of the couplings among the chemical species, energy and radiative transfer balances. As a result, high performance com- puting including sophisticated models of soot formation and oxidation has been extensively developed for the last two decades, delivering numerical simulations that can decently predict local soot concentrations in flames [4, 5, 15-18]. As the integration of highly detailed soot models into CFD codes remains tricky for most of today's computational resources, lighter semi-empirical soot production models can be used. Among these, some produced fair results, interestingly using the smoke point characteristics as an input to soot formation models [16,17].

In contrast, few studies were devoted to the fine numerical simulation of the transition from the "closed-tip" flame configuration to the "open-tip" one. To this end, Liu et al. [4] extended a CFD code that incorporates both simplified soot chemistry and radiative transfer models. These authors needed to introduce two temperature-dependent correction factors in the soot oxidation schemes to successfully simulate the smoke point for a given experimental configuration, i.e. properly reproduce the quenching at the flame tip. The authors indicated that the exact physical and chemical processes associated with the modified soot oxidation rates were not fully understood and no guarantees were given that the model would be accurate in other configurations. Thus, documenting the soot characteristics at the vicinity of the smoke point conditions could provide insights into the understanding of the phenomena governing the transition. In addition, further validation of the smoke point computation would then make it a meaningful output ruling out the need for it as an input of the simulations and poses a severe challenge to the capability and integrity of soot models.

Objectives and expected results

The PhD works will first focus on providing an experimental characterization of soot related fields at the aforementioned transition around the smoke point of steady laminar axisymmetric non-premixed flames. The experimental setup implemented by Jocher et al. [19] will be used and the flames will be established over the Santoro burner that is largely documented in the literature, especially with respect to soot [20-26]. With this configuration, soot temperature measurements using thermocouples [24], soot volume fraction, particle size, and number density [25], and morphology after soot sampling [26] have already been documented at the vicinity of the smoke point. Here, fields of both soot temperature and volume fraction covering the whole flame will be measured by the two-color Modulated Absorption/Emission (2C-MAE) technique developed by Legros et al. [27]. As an original contribution to the optical diagnostics, a third laser beam operating at a wavelength of 405 nm will be incorporated to deliver information on the distribution of local scattering coefficient attributed to soot. Doing so, the upgraded three-color MAE (3C-MAE) is expected to provide with an experimental assessment of radiative heat transfer models in flames that usually assume negligible contribution of scattering [4].

The conditions at which the flame tip opens and releases soot, i.e. does not favour soot oxidation, mainly depend on the carbon particles load produced in the flame and the temperature field at the flame tip. The oxygen content of the fuel stream has been shown to play a key role in the conditions met at the flame tip [23]. As a result, biofuels, especially oxygenated additives, will be added to the fuel stream to access a wider range of conditions for carbon release. Thus, the fuel stream composition (ethylene mixed with hydrocarbons and oxygenated additives vapours) and flow rate, oxidizer stream composition and flow rate, and pressure (1-10 atm) will be varied to assess the range of the soot characteristics that the burner can produce.

The procedure used to provide preliminary results delivered in Ref.[10] will be conducted to characterize the soot deposit sampled at the burner exhaust. Thus, laser granulometry, CHONS analysis, Raman spectroscopy, ThermoGravimetric Analysis, and a Temperature Programmed Oxidation device will deliver size distribution, elemental composition, the content in dislocated graphene layers, the content in ash, and the reactivity, respectively, of the soot produced.

The formation and growing processes of soot are partially governed by chemical reactions involving hydrocarbon additions [28]. A good knowledge of the hydrocarbon nature inside the flame at different soot formation steps can provide helpful data for the understanding of the process. Therefore, the analyses will be completed by the structure analysis of flat premixed flames stabilized on McKenna burner. Such flames are unidimensional and can be easily modeled. Consequently, a first comparison with modelling will be operated at this stage in order to evaluate the ability of a detailed combustion mechanism to allow an accurate prediction of the hydrocarbons concentration along the flames.

In a joint effort of numerical predictions, experimental soot release conditions are to be contrasted with those identified by the two-dimensional axisymmetric code CIAO, developed by Prof Pitsch's group at RWTH Aachen. This code solves the Navier-Stokes equations in the low-Mach-number limit [29,30] and can include detailed chemical mechanisms [31] together with radiative computations accounting for gas phase and soot contributions. In addition, a hybrid method of moments (HMOM) [32] allows for the prediction of soot size distribution by taking the volume and surface of the soot particles into account.

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