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Article Using in situ measurements to experimentally characterize TiO₂ nanoparticle synthesis in a turbulent isopropyl alcohol flame

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- 1 Abstract: The objective of the present work is to show the potential of in situ measurements
- ² for the investigation of nanoparticles production in turbulent spray flames. This is achieved by
- 3 considering multiple diagnostics to characterize the liquid break-up, the reactive flow and the
- ⁴ particles production in a spray burner for TiO₂ nanoparticle synthesis. The considered liquid fuel
- s is a solution of isopropyl alcohol and titanium tetraisopropoxide (TTIP) precursor. Measurements
- 6 show that shadowgraphy can be used to simultaneously localize spray and nanoparticles, light
- τ scattering allow to characterize the TiO₂ nanoparticles distribution in the flame central plane,
- and spontaneous CH* and OH* chemiluminescences as well as global light emission results can
- be used to visualize the reactive flow patterns that may differ with and without injection of
- ¹⁰ TTIP. Concerning the liquid, it is observed that is localized in a small region close to the injector
- nozzle where it is dispersed by the oxygen flow resulting in droplets. The liquid droplets rapidly
- $_{12}$ evaporate and TTIP is quasi-immediately converted to TiO₂ nanoparticles. Finally, results show
- 13 high interactions between nanoparticles and the turbulent eddies.
- 14 Keywords: In situ optical diagnostics; flame synthesis; TiO₂; turbulence

1. Introduction

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Synthesis in turbulent spray flames is today considered as a valuable alternative 16 for large-scale production of nanoparticles with a relatively low cost. Laboratory-scale 17 spray flame reactors [1–12] were therefore developed to improve our understanding of 18 nanoparticles production in these reactive flows in order to better control the characteris-19 tics and properties of the final product. For this, ex situ measurements are classically 20 performed to characterize the collected materials in terms of morphology, physical and 21 optical properties depending, for example, on operating conditions such as tempera-22 ture, pressure, and precursor concentration. However, it is expected that the properties 23 of nanoparticles produced via flame synthesis will depend on the experienced local 24 conditions governed by the flow and the flame. Therefore, it would be of interest to 25 combine classical ex situ measurements to in situ optical diagnostics classically used in 26 combustion research to understand the physical processes occurring during the flame 27 synthesis by characterizing the spatial and temporal evolution of spray, flow, flame 28 and nanoparticles. In addition, in situ measurements will allow the characterization 29 of boundary conditions necessary to perform numerical simulations [13–17] and they 30 31 provide an experimental database for their validation [9,18].

In this framework, the present study aims to prove the feasability and the great interest of in situ measurements when investigating nanoparticles production in a laboratory-scale spray flame reactor. The burner consists of a spray nozzle where the liquid fuel is atomized by an annular flow of oxygen, a circular pilot premixed ethylene/air flame and a coflow of pure N_2 . The considered liquid fuel is a solution of isopropyl alcohol and titanium tetraisopropoxide (TTIP) precursor.

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Figure 1. a) Flame luminosity without and with injection of TTIP. b) Schematic presentations of the reactor inlet and of the processes inside the reactor.

Three main processes characterize the flame: a) the break-up of the liquid jet, b) the turbulent reactive flow, and c) the production of the particles. The spatial localization of these three processes is here provided using in situ experimental measurements, classically used in combustion research: a) shadowgraphy and light scattering for the liquid phase, b) flame luminosity, CH* and OH* chemiluminescences to characterize the combustion process, and c) light scattering to localize TiO₂ nanoparticles. The paper is organized as follows. First, the experimental setup is described by presenting the flame synthesis burner and the different optical diagnostics considered

in this work. Then, the potentials and the difficulties in applying shadowgraphy and
light scattering to the characterization of nanoparticles flame synthesis are discussed.
Finally, results are presented by looking at the three different processes that characterize

⁴⁹ nanoparticles flame synthesis.

50 2. Experimental setup

51 2.1. Flame synthesis burner

The burner studied in the present work is the same as used in [2-5,15], the ParteQ 52 GMBH model LS-FSR. The burner, schematically presented in Fig. 1b, allows the sta-53 bilisation of a turbulent spray flame, whose luminosity is visualized in Fig. 1a. For 54 this, liquid isopropyl alcohol (Sigma Aldrich, C_3H_8O) is injected through a syringe in 55 the center. The liquid flow is provided by a Tuthill pump upstream of a mini-Coriolis 56 flowmeter from Bronkhorst. The imposed flow rate is 0.005 Nl/min. The liquid jet is 57 surrounded and dispersed by an annular jet of pure oxygen with a flowrate of 3 Nl/min. A premixed methane-oxygen pilot flame with an equivalence ratio of $\Phi = 0.83$ (oxygen 59 flowrate of 1.2 Nl/min and methane flowrate of 0.5 Nl/min) is needed to stabilize the non-premixed flame. The coflow consists of pure nitrogen with a flowrate of 4 Nl/min. 61 The obtained flame is visualized in Fig. 1a. As already observed in [15], the flame is 62 not perfectly axis-symmetric mainly due to a non-symmetric pilot flame as a result of 63 some geometrical imperfections of the burner. To consider TiO₂ nanoparticles production, titanium tetraisopropoxide (TTIP), Ti(OCH(CH₃)₂)₄, (Sigma Aldrich) with a purity of 65 97% is added to liquid flow in a proportion of 5 ml of TTIP for one litre of isopropyl 66 alcohol. The obtained flame is visualized in Fig. 1a. It can be observed that a more 67 luminous flame is obtained when considering injection of TTIP. 68



Figure 2. Schematic presentation of the optical setup.

69 2.2. In situ optical diagnostics

The optical setup used to perform shadowgraphy, light scattering and emission measurements is schematically presented in Fig. 2. The shadowgraph measurements 71 are performed using a red backlighting system featuring a red LED spot. The red LED 72 spot consists in a 7 cm x 9 cm rectangle of LEDs emitting at a dominant wavelength 73 of 633 nm. A frosted glass is placed between the spot and the flame to get a light as homogeneous in space as possible. The spot is fed by a direct current power supply in 75 order to avoid main current frequency interference. A Photron Fastcam SAX2 camera is 76 placed at the opposite side of the LED spot to obtain shadowgraphy images of the flame. 77 It is equipped with a Nikon 105mm f/2.8 lens and a 20 mm extension ring. Images of 78 1024x1024 pixels are obtained with a resolution of 62 μ m/pixel. The signal acquisition 79 gate width is 100 μ s. 80 81

A YAG Surelite 400 mJ Continuum laser at 532 *nm* wavelength is used for the light scattering on the solid particles. A set of two lenses creates a laser sheet of 70 mm height 82 and about 300 μ m thickness, which passes through the burner central axis. The scattered 83 light is captured by a Teledyne Princeton PIMAX4 camera (1024 * 1024 pixels) equipped 84 with a Nikon lens 100F/1.8 and a 20 mm extension ring. It has a spatial resolution of 62 μ m/pixel. A Semrock FF01 530nm FWHM 11 nm filter allows the observation of only 86 light scattering. Both the camera and the laser are synchronized via a pulse generatore BNC575. The images are captured with no delay and a gate width of 15 ns. 88 A second Teledyne Princeton PIMAX camera equipped with a Sodern UV lens 100F/2.8 is used for measurements of flame global spontaneous emission as well as CH* 90 and OH* emissions. The spatial resolution is 95 μ m/pixel. For flame global spontaneous 91 emission, no filter is used on the camera and the exposure time is adjusted in order to not 92 saturate the gray levels (5 μ s). Regarding the OH* spontaneous emission, an Asahi 310 93 nm filter (96SA02), FWHM 10.00 nm is used in front of the camera lens. The exposure 94 time is 30 µs. For CH* spontaneous emission, an Asahi 430 nm filter (F0102), FWHM 95

10.00 nm filter is used and an exposure time of 15 μ s is retained.

Time-averaged results for all measurements are obtained by subtracting the background and considering 500 images.

⁹⁹ 3. Using shadowgraphy and light scattering diagnostics to characterize flame ¹⁰⁰ synthesis

Several phenomena can be visualized using the shadowgraphy measurements as illustrated in Fig. 3a. First of all, when considering the non-reacting cold case, the presence of the liquid jet and of the spray can be detected since the objects between the light source and the camera appear the darker the more they absorb the light. Similarly, the presence of liquid jet is detected in both reacting cases without and with injection of TTIP. It can be observed that the liquid phase occupies a smaller region, compared to the cold case, due to its quick evaporation due to high flame temperature.

In the reactive case, with the injection of TTIP, spots of light due to diffraction of partially transparent TiO₂ nanoparticles can also be observed. Then, it is possible to



Figure 3. Instantaneous images obtained by (a) shadowgraphy and (b) light scattering, without and with injection of TTIP. Results for the non-reacting cold case with shadowgraphy are also presented.

discriminate spray from TiO₂ nanoparticles by considering dark or bright information.
Therefore, thanks to the shadowgraphy, it is possible to get simultaneous information on
the localization of both spray and of TiO₂ nanoparticles.

Since the shadography measurements provide line-of-sight-integrated informa-113 tion, light scattering measurements were also performed to investigate spray and TiO_2 114 nanoparticles distribution at the burner central plane. Instantaneous images for both 115 cases with and without injection of TTIP are presented in Fig. 3b. Although planar 116 information can be obtained with this technique, however, a rigorous discrimination 117 between the signals from spray and TiO_2 nanoparticles is not straightforward. It has 118 been observed that, in the region close to the liquid injection, the contribution from the 119 liquid spray scattering is predominant compared to the one from nanoparticles. There-120 fore, it is assumed in the following that, in the spray zone close to the burner, a high 121 intensity signal corresponds to spray light scattering, whereas low intensity corresponds 122 to TiO₂ nanoparticles. Even if such criterion is arbitrary, the complementary use of 123 shadowgraphy allows to identify the region where the liquid phase is expected to be 124 observed (in our case for a height above the burner z < 2 cm). Indeed in this region, 125 results from light scattering should be analyzed with caution, but beyond this region, 126 light scattering information can be used to localize the presence of TiO₂ particles. 127

128 4. Characterization of spray flame synthesis

The main processes occurring during the flame synthesis, schematically presented in Fig. 1b, are described here thanks to in situ optical diagnostics, classically used in combustion research, comparing results on flames with and without injection of TTIP.



Figure 4. Localization of liquid phase (blue color) and TiO_2 nanoparticles (brown palette) via (a) shadowgraphy, and (b) light scattering. Time-averaged results (left) without and (right) with injection of TTIP are presented.



Figure 5. (a) Instantaneous and (b) time-averaged images of line-of-sight-integrated global emission for the reactive cases (left) without and (right) with injection of TTIP.

132 4.1. Liquid injection and spray

Thanks to shadowgraphy and light scattering measurements, the presence of liquid can be investigated. When looking at the instantaneous results of Fig. 3, the presence of a central liquid jet core is observed. The liquid is localized in a small region close to the injector nozzle due to the effect of the dispersion oxygen flow, which leads to the break up of the liquid jet into droplets, together with the effect of the flame high temperature, which results in a rapid evaporation. Occasionally, big droplets can be observed at higher heights above the burner.

It should be noted that some differences are observed between the two techniques. In particular, a dense cylindrical liquid jet seems to be detected by light scattering whereas the atomization seems to occur more rapidly from shadowgraphy results. However, it has to be reminded that the two systems neither present the same sensitivity nor the same resolution of the liquid structures. Moreover, line-of-sight-integrated measurements are provided by shadowgraphy, whereas light scattering gives access to planar information. Finally, light scattering results may be affected by the fact that both spray and TiO₂ nanoparticles are simultaneouslydetected.

Time-averaged shadowgraphy and light scattering results are presented in Fig. 4 for the flames without and with injection of TTIP. A slightly shorter spray region is identified in the case of the flame with TTIP. However, no other significant differences are observed so that it can be deduced that the spray region is correctly identified by the light scattering technique even in the presence of nanoparticles. Therefore, the differences between results from light scattering and shadowgraphy are most probably due to the intrinsic specificity of these two techniques.

Even if a more detailed characterization of the performances of these techniques 155 in the context of flame synthesis is desirable, some common conclusions on the spray 156 process can already be drawn. First, high fluctuations of the spray position are observed 157 (not shown). Second, results are not symmetric, possibly due to the difficulty in obtaining 158 a perfect centering of the liquid injection syringe in the dispersion system. Third, TiO_2 159 nanoparticles are formed close the spray, indicating that the nanoparticles production is an extremely fast process occuring once the TTIP precursor has evaporated. Finally, it 161 can be said that the spray is not likely to be found for z > 2 cm, so that in this region light 162 scattering from spray can be considered as negligible compared to nanoparticles contri-163 bution. Therefore, results on the localization of TiO₂ nanoparticles can be considered with confidence for z > 2 cm. 165



Figure 6. Time-averaged line-of-sight-integrated of (a) OH* and (b) CH* emission for the reactive cases (left) without and (right) with injection of TTIP.

166 4.2. Flame

The combustion process is investigated here by analyzing images of flame global spontaneous emission (Fig. 5) as well as CH* and OH* chemiluminescences (Fig. 7). The global spontaneous emission from the flame contains information on the whole flame emission, while CH* and OH* chemiluminescences can be used to localize the heat release zone. In the presented case, the signal from global spontaneous emission is generally 10 times more intense than the one from OH* and CH*.

Looking at the instantaneous global emission results, Fig. 5a, a turbulent flame structure can be recognized even if these measurements provide line-of-sight-integrated information. When considering time-averaged results, Fig. 5b, it can be noticed that the symmetry of the fields is not perfect, similarly to the results for spray in Fig. 3.

Results are quite different between the two cases with and without injection of TTIP, indicating that the addition of TTIP has a non-negligible effect on global spontaneous 178 emission, as already deduced from Fig. 1a. When looking at the case without TTIP, the 179 most relevant emission contribution due to the isopropyl flame is located along the 180 central line at small height above the burner (z < 1 cm). The pilot flame is identified by 181 the small conical emission region localized close to the burner tip and it only slightly 182 contributes to the flame emission. In the case with injection of TTIP (Fig. 5b), the 183 maximum values of emission are found far above the burner (0.5 cm < z < 1.5 cm) due 184 to the presence of nanoparticles. In this case, spontaneous emission is the result of both 185 flame and nanoparticles emissions. The maximum values of spontaneous emission for 186 the case with injection of TTIP are higher by a factor of 10, compared to the case without 187 injection of TTIP. 188

Time-averaged fields of OH* and CH* chemiluminescences are presented in Fig. 6. 180 Concerning results without injection of TTIP, CH* and OH* chemiluminescence signals 19 present a similar spatial evolution compared to global emission. Most of the heat is 191 expected to be released close to the region where spray evaporation occurs (z < 2 cm), 192 with a maximum located at z < 1 cm. Post-combustion processes are observed up to 193 $z \approx 5$ cm. Close to the injector, a lower signal intensity is measured compared to the central region, possibly indicating that the pilot flame only slightly contributes to the 195 global heat release even if it is essential for the flame stabilization. Results with injection 196 of TTIP are qualitatively similar to those without TTIP, even if more intense signals are 197 observed for the TTIP case. This is probably due to the fact that the addition of TTIP 198 leads to an increase of carbon atoms compared to a pure isopropyl alcohol flame. By 199 comparing these results with those on global emission for the TTIP case in Fig. 5, it can 200



Figure 7. Planar information are extracted using the Abel-inversion on time-averaged results from OH* chemiluminescence for the reactive cases (left) without and (right) with injection of TTIP.

be confirmed that the maximum of global emission at z > 1 cm is due to the presence of particles.

Classically, time-averaged line-of-sight integrated results could be transformed 203 using an Abel-inversion to obtain 2-D planar information. Since the investigated flame 204 is not quite axis-symmetric, as can be deduced by looking for example at the CH* results in Fig. 6b), caution should be paid when analysis Abel-inverted results. An example 206 of planar results is presented in Fig. 7 considering only the right half-side of the time-207 averaged results from OH* chemiluminescence. When looking at 2-D planar fields, a 208 lower signal intensity is measured close to the injector compared to the central region. 209 Therefore, it is quite evident by looking at 2-D fields that the pilot flame only slightly 210 contributes to the global heat release even if it is essential for the flame stabilization. 211 Globally, similar conclusions can be deduced compared to line-of-sight integrated results 212 in terms of localization of maximum value of OH* signal and effect of TTIP addition on 213 OH* emission. 214

215 4.3. Particles production

Figure 8 presents light scattering measurements of TiO_2 nanoparticles by gathering 216 random collections of data at different vertical positions above the burner. As mentioned 217 above, the presence of TiO₂ nanoparticles can be analyzed by looking at both shadowg-218 raphy and light scattering fields. When looking to results close to the injector (Fig. 4), it 219 can be seen that nanoparticles appear in the close proximity of the spray. This indicates 220 that, once the liquid TTIP precursor has evaporated, it is rapidly converted into solid 221 TiO_2 particles, confirming that TiO_2 production is governed by fast reactions. Once the 222 particles formed, their localization seems to be strongly governed by turbulent eddies, as 223 it can be observed from the instantaneous results of light scattering close to the injector 224 (Fig. 4b) and along the flame (Fig. 8a). Then, TiO₂ particles mainly concentrate along thin ligaments that are stretched and deformed by the turbulent flow eddies and are 226 finally convected downstream the combustion region (z > 4 cm). 227

Far downstream of the burner (z > 7 cm), a more homogeneous spatial distribution of TiO₂ particles is observed due to turbulent mixing. Time-averaged results of light scattering are presented in Fig. 8b. A very intense signal is observed close to the burner, which decreases downstream the post-flame region. This high light scattering region seems to coincide with the high flame luminosity zone in Fig. 1a. The light scattering



Figure 8. Localization of TiO₂ nanoparticles via light scattering measurements. Instantaneous (left) and time-averaged (right) fields. Time-averaged field is reconstructed by assembling series of measurements at six vertical positions of the laser sheet.

signal depends on particle size and number density. Since the size of the particles is not
expected to decrease along the height above the burner, the light scattering field seems to
indicate that the nanoparticles are generated close the spray region in large number and
that the particles number density subsequently decreases due to collisional processes.
Even if the distribution of the light scattering signal is not symmetric close to the burner
(Fig. 4b) due a non axis-symmetric flame, its time-averaged distribution becomes rapidly
symmetric, probably due to the turbulent transport of the particles downstream.

240 5. Conclusion

The objective of the present work was to demonstrate the interest of in situ optical diagnostics classically used in combustion research for the investigation of TiO₂ ananoparticles synthesis in turbulent spray flames. Shadowgraphy, light scattering, and global flame luminosity as well as CH* and OH* chemiluminescence measurements were employed in order to study the three main processes that characterize the spray flame. In this way, the liquid break-up, the reactive flow and the TiO₂ nanoparticles production were analyzed.

Shadowgraphy measurements showed that it was possible to simultaneously localize the liquid phase and the nanoparticles. Light scattering results allowed to characterize 249 the TiO_2 nanoparticles distribution in the flame central plane. The liquid flow is localized 250 in a small region close to the injector nozzle where it is dispersed by the oxygen flow 251 resulting in droplets. The liquid droplets rapidly evaporate due to high temperature 252 of the flame. When TTIP is added to the liquid flow, right after its evaporation and 253 due to its high reactivity, it is immediately converted to TiO_2 nanoparticles. Global 254 spontaneous emission is quite different when considering TTIP compared to the flame 255 without TTIP. In specific, when TTIP is added, maximum emissions are observed far 256 above the burner showing the non-negligible contribution of TiO_2 particles emissions. 257 On the contrary, even if CH* and OH* chemiluminescence signals are more intense when 258 adding TTIP, the signals are qualitatively in agreement with the flame without TTIP. 259 Finally shadowgraphy and light scattering results at different hights above the burner 260 showed high interactions between nanoparticles and the turbulent eddies. Even if in 261 future works an optimization of theses techniques to flame synthesis is desirable, in situ 262 optical diagnostics from combustion research can be used to provide a new insight on 263 flame synthesis, complementary to ex situ measurements. 264

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