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GAS-LIQUID MASS TRANSFER CHARACTERIZATION IN A THIN SHRINKING FILM AT AN ATOMIZATION NOZZLE

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Abstract

In this paper, a light absorption method is applied to estimate the thickness of an atomizing liquid film at microscale that exits a spraying nozzle. By using a dioxygen sensitive dye, called resazurin, it is also possible to determine the local profile of dioxygen concentration resulting from the gas-liquid transfer from air into the liquid film. The method relies on the use of the well-known Beer-Lambert law, the linearity of which has been experimentally proved for the optical system and the dye concentration used in this study. From thickness and dye concentration measurements in the liquid film formed at the outlet of the nozzle, a mass transfer analysis is performed, providing a local description of the dioxygen mass transfer (concentration fluxes, etc.) occurring in this film. This optical method, leading to a dual measurement of thickness and mass transfer, is the first to be successfully implemented in this type of thin liquid film in sprays ($\approx 30 \mu\text{m}$) at microscale and with such high velocities ($\approx 8 \text{ m/s}$). The method is non-invasive and does not disturb the flow, in comparison with classical liquid phase measurements where the liquid is collected to be titrated. The values of the mass transfer coefficients, k_L , deduced from our analysis for the liquid film ($2.2 \times 10^{-3} - 1.2 \times 10^{-2} \text{ m/s}$) are consistent with global measurements already obtained, validating our measurement and giving more insight into the mass transfer occurring in this film.

Keywords: Film thickness, mass transfer coefficient, concentration measurement, resazurin, spray, , , light absorption

1. Introduction

29 Spraying processes have been widespread in chemical and industrial applications for years (Ashgriz, 2011).
30 They convert a bulk liquid into dispersions of small droplets in a gaseous environment by giving high
31 velocity to the liquid relative to the surrounding gas. Using kinetic energy, spraying offers a high interfacial
32 area of the dispersed liquid, which leads to many applications in combustion, crop protection, gas treatment
33 and also coating of materials (Lefebvre and McDonnell, 2017; Lefebvre, 1989).

34 The process of spray formation can be described as follows: the liquid exits the orifice of the nozzle and
35 forms a thin liquid film a few centimeters long. The liquid film undergoes instabilities due to friction with
36 the gas phase, leading to growing waves in its core. Once the waves reach a critical amplitude, a part of the
37 liquid film breaks into cylindrical ligaments. These ligaments are also torn apart by friction and disrupt into
38 droplets. The liquid in this region has high velocity, growing instabilities in its core, and a window of
39 investigation that is quite small (Lefebvre, 1989; Reitz, 1982). The main parameters used for the
40 characterization of the spray, such as droplet diameters and velocities, length and width of the liquid film,
41 and spray angles, are easily obtained by image acquisition (Dumouchel, 2008; Fansler and Parrish, 2015).
42 The thickness of flowing liquids has been assessed in several ways, using: a conductance method (Kim et
43 al., 2009; Suyari and Lefebvre, 1986), a needle contact method (Rizk and Lefebvre, 1980), and optical
44 methods. Optical methods have the advantage of not disturbing the flow and of bringing together various
45 techniques, including interferometry methods (Koralek et al., 2018) and light absorption methods (Mendez
46 et al., 2016; Zhang et al., 2000).

47 The large interfacial area and the friction between the dispersed phase and the gas phase, produced by the
48 spray, promote the diffusion of solute between phases. For this reason, spraying processes are very often
49 used in chemical engineering to perform gas depollution since the sprayed liquid absorbs compounds from
50 the gas phase, performing volatile organic compound removal, CO₂ capture, H₂S decontamination, etc. The
51 efficiencies of such processes mainly depend on the control of the gas/liquid contact (quality of the
52 atomization, gas flow, etc.) and chemical composition of the phases (Ashgriz, 2011; Hariz et al., 2017; Tatin

53 et al., 2015).

54 Mass transfer in spray is commonly well understood when considering liquid droplets exchanging solutes
55 with the gas phase, and many correlations have been proposed to predict the extent of the transfer (Hegely
56 et al., 2017; Lépinasse et al., 2012). Several studies have focused on the liquid film behavior and revealed
57 that the atomizing liquid film that produces the droplets seems to enhance the mass transfer due to its
58 hydrodynamic conditions and interfacial area (Canado et al., 2020; Lin et al., 1977; Simpson and Lynn,
59 1977; Yeh and Rochelle, 2003). Mass transfer enhancement during the formation stage of droplets or
60 bubbles has also been reported, showing the importance of taking the formation region into consideration
61 for mass transfer applications (Wegener et al., 2009; Xu et al., 2008; Yang et al., 2016).

62 To quantify the mass transfer enhancement during the formation stage, solute measurements must be made
63 in the region where the droplets are formed. The difficulty of such measurements lies in avoiding any
64 disturbances of the liquid flow in order to measure the composition of the liquid correctly. Although many
65 titration methods exist to quantify a given solute in a liquid, methods giving direct access to the solute
66 quantification without liquid collection, such as Raman scattering spectroscopy, rainbow refractometry, or
67 laser induced fluorescence, are rare or difficult to implement (Lebrun et al., 2021; Lemoine and Castanet,
68 2013). Liquid collection methods report the global behavior of the mass transfer process, but they lack
69 spatial and time resolution since the liquid collector volume varies with the collection of liquid and the
70 titration is delayed with respect to the moment of collection. Moreover, they involve end effects such as
71 wall collisions, splashes and eddies that can lead to overestimation of the mass transfer. Although various
72 methods are reported in the literature for measuring the temperature of droplets (Brübach et al., 2006;
73 Strizhak et al., 2020; Volkov and Strizhak, 2018; Xue and Zhang, 2018) and their composition (Shao et al.,
74 2012; Srinivasan and Aiken, 1988), no reliable techniques have been proposed for in situ measurement of
75 the mass transfer in the region of the liquid film that produces the droplets.

76 A recent method for oxygen mass transfer visualization and measurement has been successfully applied to
77 several gas-liquid-solid contactors (Dietrich et al., 2019, 2013; Dietrich and Hebrard, 2018; Kherbeche et

78 al., 2020, 2013; Mei et al., 2020; Yang et al., 2016). It relies on the light absorption of a dioxygen sensitive
79 dye. In presence of glucose and sodium hydroxide, the dye can be oxidized (e.g., by dissolved dioxygen),
80 and this oxidation leads to a new form of the dye, which absorbs light of a different wavelength. Then, from
81 light absorption, the quantity of oxidized dye, and thence the quantity of dioxygen that has been transferred
82 and has reacted with the dye, can be determined. This method provides solute quantification without
83 disturbing the flow and offers a fun way to visualize the mass transfer.

84 To the best of our knowledge, there is no optical technique devoted to the dual measurement of thickness
85 and concentration in a sprayed film. Light absorption could be a suitable solution for investigating both
86 hydrodynamics and mass transfer in such a condition. Therefore, the objective of the present study is to
87 implement a light absorption technique for the first dual and simultaneous measurement of mass transfer
88 and film thickness in a free-flowing liquid film produced by a converging fan nozzle before its atomization
89 into droplets.

90 **2. Materials**

91 ***2.1. Measurement strategy***

92 The method presented is based on the use of an oxygen-sensitive dye, rezasurin (CAS n°62758-13-8). This
93 organic chemical compound possesses an interesting property: if subjected to an oxidation/reduction
94 reaction, it produces an intense color when oxidized whereas it is colorless in its reduced form. Note that
95 the oxidation reaction is extremely fast compared to the reduction reaction, which is slow (Yang et al.,
96 2017).

97 Initially, a solution of resazurin (RZ) in water is dark blue, as shown in Fig.1. In presence of glucose and
98 sodium hydroxide, the resazurin is reduced to its resorufin (RSO) form, which appears pink in solution.
99 This reduction is quite slow and cannot be reversed by oxidation. Further reduction of the resorufin leads
100 to the formation of dihydroresorufin (DHR), which is colorless in solution and is extremely sensitive to
101 oxidation.

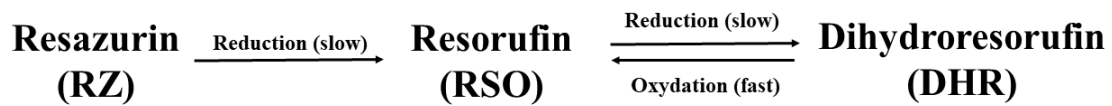
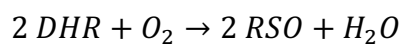


Figure 1: Oxidation and reduction reactions for resazurin and its reduced forms.

Any dissolved oxygen in the liquid will react with the DHR to produce RSO and its pink color. As can be seen at the top of the flask of DHR in Fig.1, atmospheric dioxygen dissolves and reacts with DHR to produce a pink layer of RSO. In this way, light absorption through the liquid enables a quantification of RSO, which can be associated with a quantification of the dissolved dioxygen that has transferred and reacted, given that the oxidation stoichiometry is known:



When spraying a DHR solution in air, O_2 from the gas phase is expected to transfer into the solution and to produce pink RSO by reaction. The present method aims to quantify the “pink” produced by the appearance of RSO along the atomizing thin liquid film that leaves a nozzle.

2.2. Chemicals

Table 1 lists the different solutions prepared and sprayed to perform a complete experimental run:

Solution name	[Rz]	[Glucose]	[NaOH]	Air bubbling before spraying
	(mg/L)	(g/L)	(g/L)	
Ref	0	10	10	No

Experimental	200	10	10	No
Calibration-10 mgO ₂ ^{eq} /L	200	10	10	Yes
Calibration-6 mgO ₂ ^{eq} /L	120	6	6	Yes
Calibration-3 mgO ₂ ^{eq} /L	54	2.7	2.7	Yes
Calibration-2 mgO ₂ ^{eq} /L	40	2	2	Yes

Table 1. Composition of the solutions prepared and sprayed.

The reference solution “Ref” was composed of 10 g/L of glucose and 10 g/L of sodium hydroxide dissolved in distilled water like all the other solutions but it did not contain any dye. This solution was colorless.

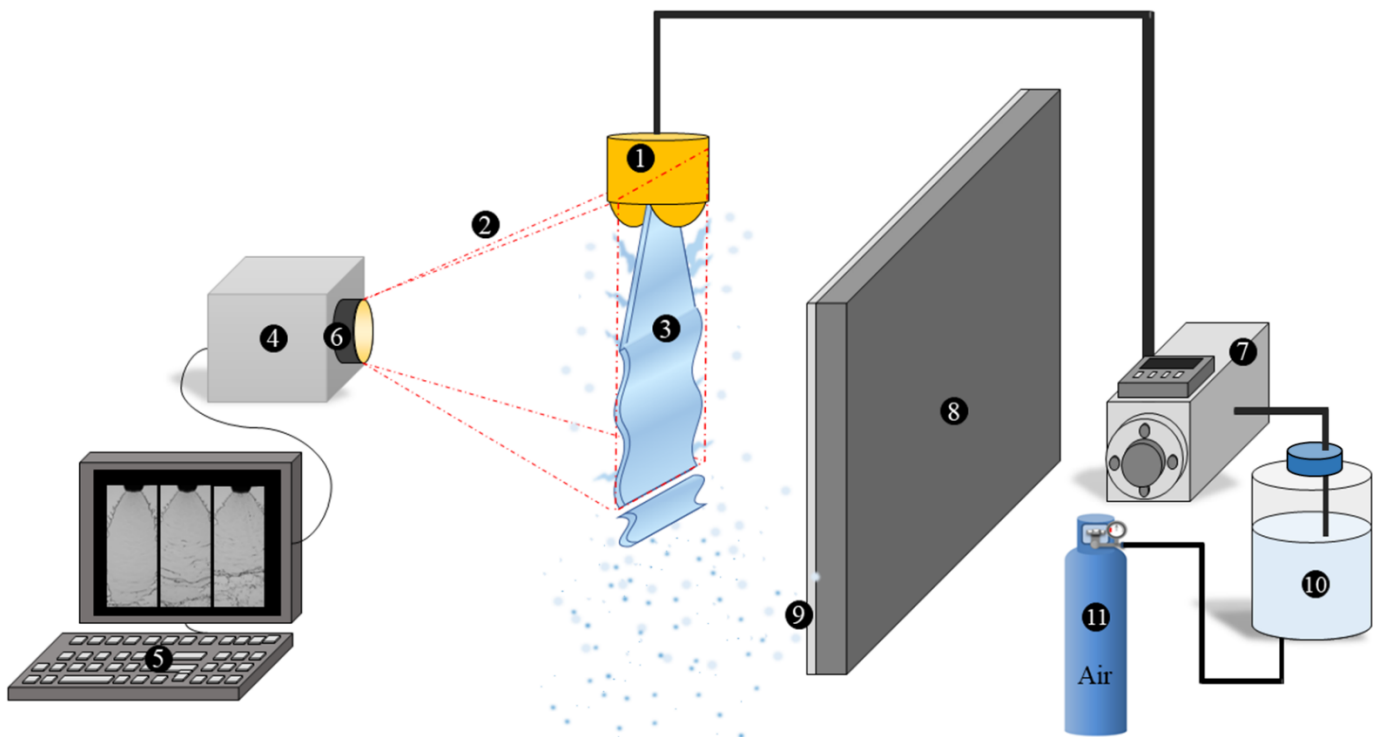
The “Experimental solution” was prepared by dissolving 200 mg of RZ, 10 g of NaOH and 10 g of Glucose in a 1 L flask of distilled water. Around one hour later, the solution turned from blue to colorless. At this step, the colorless DHR solution was very reactive with O₂. When the Experimental solution was sprayed, atmospheric O₂ was expected to transfer into the liquid film and convert the colorless DHR into pink RSO.

The “Calibration-10 mgO₂^{eq}/L solution” was prepared in the same way as the Experimental solution except that it was fully oxidized by air bubbling before spraying, to convert all the DHR present in the solution into RSO. In this way, the concentration of RSO in the solution was homogeneous and ensured that the RSO concentration in the liquid film was constant when the calibration solutions were sprayed. The concentration of RSO is expressed in “O₂^{eq}”. For instance, using the stoichiometry of the oxidation, 120 mg/L of DHR requires the transfer and the reaction of 6 mg/L of dioxygen to fully oxidize the colorless DHR into pink RSO. Several concentrations were prepared from the “Calibration-10mgO₂^{eq}/L” by dilution to make standard curves to verify linearity between absorbance, RSO concentration and thickness of the liquid film (Beer-Lambert). The standard curves obtained are presented in the “procedure validation” part.

2.3. Image acquisition

To observe any appearance of pink color in the free-flowing liquid film, solutions had to be sprayed and the light crossing the liquid had to be recorded. The experimental set-up shown in Fig.2 was used to obtain images of the free-flowing liquid film atomizing different solutions. First, the solution was contained in a

135 tank, and a pump (WT3000-1JA, Longer precision pump Co. Ltd, China) sent the liquid to a nozzle that
136 atomized it in front of a CMOS camera (acA9120 – 155um, Basler AG, Germany) equipped with a lens
137 (Nikon AF micro Nikkor f/2.8 lens 60mm). The air feed connected to the tank is used to perform the air
138 bubbling of the calibration solutions to reach complete states of oxidation before spraying. The camera took
139 1920×800 pixel images with an exposure time of 20 μ s at 100 frames per second. Thus, the spatial resolution
140 was 26 μ m/pixel. The light source was a LED panel placed behind the liquid sheet, producing white light.
141 A filter located on the LED panel ensured that the light reaching the camera was almost monochromatic,
142 around 550 nm (FWHM=[540nm-575nm]). 500mL beakers were placed under the nozzle to recover the
143 sprayed solution. A fan spray nozzle (AFX-80-02, Nozal, France) with an orifice 1 mm in diameter was
144 used to produce a spray with an 80° angle and droplets around 0.6 mm in diameter. In the range of our
145 operating conditions, the AFX nozzle had the advantage of producing a flat liquid film that could be
146 matched with the focal plane of the CMOS camera.



(The nozzle and the liquid film are not to scale compared to the equipment)

147

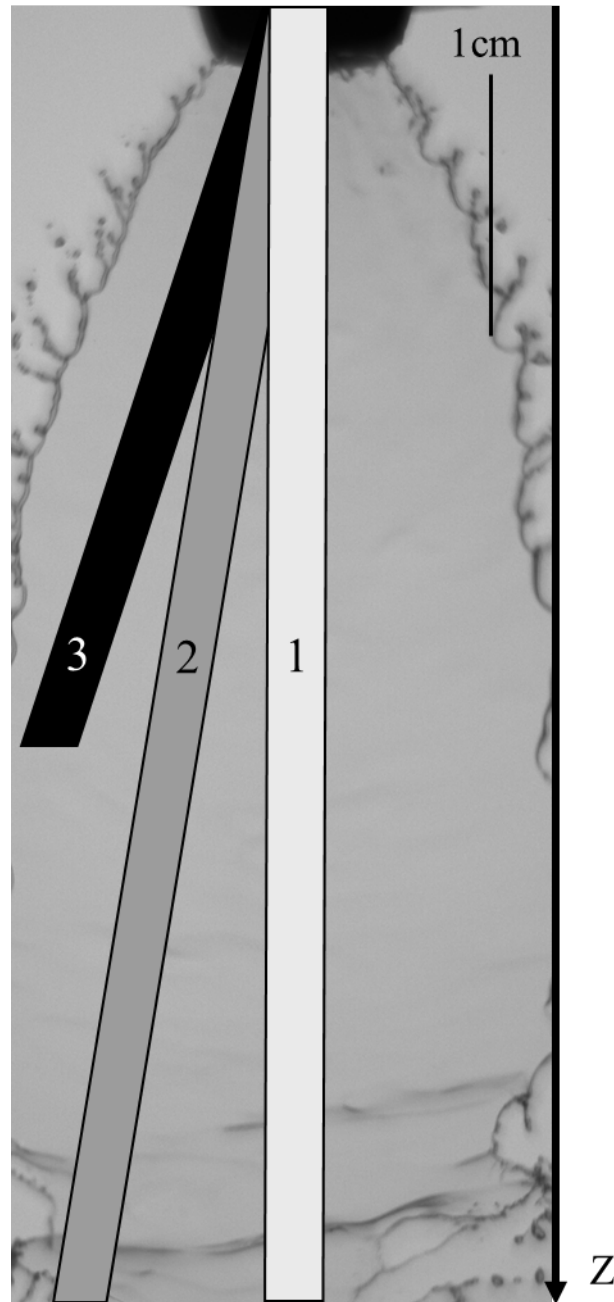
148 Fig.2: Experimental setup for light absorption through the liquid film produced by a nozzle before its
149 atomization in droplets. Nozzle (1), acquisition window (2), liquid film (3), CMOS camera (4), computer
150 (5), lens (6), pump (7), LED panel (8), 550 nm filter (9), 1.5L Bottle (10), air feed (11)

151 Experiments were repeated 6 times. A complete run of an experiment consisted in spraying all the solutions
152 described in the chemical part and recording the images.

153 3. Methods

154 3.1. Determination of light absorption

155 For each solution sprayed, 500 images were recorded with the camera, and 3 different study regions were
156 defined in the liquid film as shown in Fig. 3.



157

158 Fig. 3: Image of the liquid film obtained at 22.6 L/h with the experimental setup and the three different

159 study regions.

160 Each region has a 100pixel-width and a 1920pixel-length. For each z pixel on the length of the region, the
161 100 pixels on the width are averaged to obtain a representative value of the intensity in the core of the study
162 region.

163 Thus, each image i had its own intensity evolution along the film $I_j^i(z) = \sum_{w=1}^{w=100} \frac{I_j^i(z,w)}{100}$ for a given
164 sprayed solution j , with w the w^{th} pixel in the width of the region. Then the intensity profile for a sprayed
165 solution was defined as the mean intensity of all the images:

$$I_j(z) = \frac{\sum_{i=1}^{i=500} I_j^i(z)}{500} .$$

(Eq.1)

168 A complete run consisted of recording the intensity profile of the reference solution I_{ref} , of the calibration
169 solutions I_{calib10} , I_{calib6} , I_{calib3} , I_{calib2} and of the experimental solution I_{exp} .

170 Note that when we refers to “distance in the liquid film”, we mean the actual distance travelled on a given
171 streamline, respecting the inclination of region 2 and 3.

172 3.1.1. Beer-Lambert law

173 The present method relied on the use of the well-known Beer-Lambert law (Buijs and Maurice, 1969;
174 Swinehart, 1962). The light absorption of a liquid is a function of the thickness of liquid crossed by the
175 light and of the dye concentration for a given wavelength:

$$A_j(z) = \log\left(\frac{I_{\text{ref}}(z)}{I_j(z)}\right) = \varepsilon \delta(z) C_{\text{RSO}}(z)$$

(Eq.2)

178
179 With $A_j(z)$ the absorbance (-) of the liquid sheet at the z position for the j condition, $I_{\text{ref}}(z)$ the
180 reference intensity at z , $I_j(z)$ the intensity at z for the j solution, ε the molar attenuation coefficient ($\text{M}^{-1}\cdot\text{cm}^{-1}$), $\delta(z)$ the liquid thickness crossed by the light at z (cm) and $C_{\text{RSO}}(z)$ the dye concentration in the
181 liquid at z (M).
182

183 When light from the LED panel crossed the solution, some light rays were refracted at the gas-liquid

184 interface due to the refractive index difference. This decreased the intensity of the light received by the
185 camera after the liquid sheet. For solutions containing dye, light intensity decrease was expected to be
186 caused by both refraction at the interface and light absorption by the dye. The reference solution served to
187 extract the light intensity decrease due only to the presence of the dye. Its role was the same as that played
188 by the reference solution when measuring the absorbance in a conventional spectrophotometer.
189 The absorbance was then defined as shown in Eq.2, and one goal of the study was to find the linear
190 relationship between absorbance, thickness, and concentration. If it was verified for our optical system, it
191 would then be possible to access the parameters mentioned above from an absorbance measurement of the
192 liquid film. This verification is presented in the “procedure validation” part.

193 3.1.2. Thickness measurement

194 Thickness measurements were performed by spraying the “Calibration” solutions that had a homogenous
195 concentration of dye $C_{RSO,j}$. With those solutions, no reaction of DHR with atmospheric O_2 was expected
196 during spraying since all the DHR had been consumed by air bubbling beforehand. Considering the Beer-
197 Lambert law, the thickness of a dye liquid crossed by a light beam can be expressed as:

$$198 \quad \delta_j(z) = \frac{A_{calib,j}(z)}{\varepsilon C_{RSO,j}} \quad (Eq.3)$$

200 $A_{calib,j}$ is the absorbance determined with Eq.2 for the RSO concentration of the j solution. The molar
201 attenuation coefficient was determined by making standard curves of diluted calibration solutions with
202 absorbance measurements made in cuvettes using a conventional spectrophotometer (Jasco V-630,
203 Germany). A complete run of an experiment was performed by spraying the 4 Calibration solutions of
204 known concentrations $C_{RSO,j}$ (10, 6, 3 and 2 mg O_2^{eq} /L). It was assumed that the concentration of RSO in
205 the thickness of the liquid was homogeneous.

206 3.1.3. RSO concentration measurements

207 When the Experimental solution was sprayed, pink RSO was expected to appear along the liquid film due
208 to transfer of atmospheric O_2 and reaction with the DHR in the liquid.

209 The RSO concentration appearing in the liquid film was deduced using the Beer-Lambert law:

$$C_{RSO}(z) = \frac{A_{Exp}(z)}{\varepsilon \overline{\delta(z)}}$$

(Eq.4)

with $\overline{\delta(z)}$ the average thickness profile obtained by averaging all the thickness profiles determined by Eq.3, and A_{Exp} the absorbance determined with Eq.2 for the Experimental solution.

3.1.4. Equivalent dioxygen transferred and mass transfer coefficient

From the stoichiometry of the oxidation reaction, and assuming that enough DHR was present in the solution, it was possible to determine the quantity of dioxygen that had reacted with the DHR to produce the profile of RSO concentration in the liquid film. Then, once the RSO concentration profile was known, the equivalent dioxygen concentration profile that explained the appearance of the RSO was expressed:

$$[O_2]_{eq}(z) = \frac{C_{RSO}(z)}{2} = \frac{A_{DHR,j}(z)}{2 \varepsilon \overline{\delta(z)}}$$

(Eq.5)

Using the equivalent dioxygen concentration profile in the liquid film, the mass transfer coefficient k_L can be determined. Considering an elementary volume of the liquid film, the mass balance between the inlet and outlet of this volume along the z-axis can be written:

$$k_L dS ([O_2]^* - [O_2]) = Q([O_2]_{inlet} + d[O_2]) - Q[O_2]_{inlet}$$

(Eq.6)

with dS the area of the interface of the elementary volume in m^2 , $[O_2]^*$ the saturation concentration of dioxygen in the liquid at ambient pressure and temperature in mg/L , $[O_2]$ the actual dioxygen concentration in the elementary volume, Q the liquid flowrate in m^3/s , $d[O_2]$ the recorded variation of dioxygen concentration between the inlet and the outlet of the elementary volume, and k_L the liquid side mass transfer coefficient in m/s . It was assumed here that concentration in the liquid film was homogeneous along the width and through the thickness of the elementary volume. The concentration change was assumed to concern the z-direction only.

Then the mass transfer coefficient can be expressed as:

$$k_L = \frac{Q}{dS} \frac{d[O_2]}{([O_2]^* - [O_2])} \quad (\text{Eq.7})$$

The elementary surface dS was assumed to be

$$dS = 2 w(z) \times dz \quad (\text{Eq.8})$$

with $w(z)$ the width between two edges of the liquid film and dz the distance between two pixels on the z-axis.

The width profile along the z-axis, $w(z)$, was determined by averaging the distance between the edges of the liquid film using an edge detection algorithm on 50 images. Note that the surface offered by the two sides of the liquid film ($2 z \times \delta(z)$) was not considered for the surface calculation as it is very small compared to the regular faces.

The actual concentration of dioxygen was expected to be null in the liquid due to the reaction of the transferred dioxygen with the DHR present in the liquid, and oxygen concentration in air is assumed to be constant. Eq.7 can be simplified to determine a local mass transfer coefficient from the concentration variation $d[O_2]$ observed between two pixels dz :

$$k_L = \frac{d[O_2]}{dz} \frac{Q}{2 w(z) [O_2]^*} \quad (\text{Eq.9})$$

Integration of Eq.9 allowed a global mass transfer coefficient, able to represent the whole liquid film, to be determined:

$$\bar{k}_L = Q \frac{[O_2]_{outlet} - [O_2]_{inlet}}{2 \overline{w(z)} [O_2]^* Z} \quad (\text{Eq.10})$$

with Z the length of the optical window (cm).

3.1.5. Dimensionless numbers

Mass transfer and hydrodynamics are commonly related using correlations that involve the use of

258 dimensionless numbers such as the Sherwood and Reynolds numbers. The Sherwood number indicates the
259 strength of the mass transfer of a solute compared to its diffusion in the liquid of interest:

$$260 \quad Sh = \frac{k_L}{D_{O_2/H_2O}} \bar{\delta}$$

261 (Eq.11)

262 with $\bar{\delta}$ the mean value of the liquid thickness averaged along the film. The thickness of the liquid was
263 considered as the characteristic length since the small thicknesses of the liquid film could promote the liquid
264 film renewal responsible for enhancing the diffusion of the solute. The Reynolds number describing the
265 nature of the flow was defined as:

$$266 \quad Re = U \frac{\rho_{H_2O}}{\mu_{H_2O}} \bar{\delta}$$

267 (Eq.12)

268 with ρ_{H_2O} and μ_{H_2O} the density and the dynamic viscosity of the water, respectively, and U the liquid
269 film velocity determined considering the flowrate of liquid passing through the 1 mm orifice of the nozzle:

$$270 \quad U = \frac{Q}{\frac{\pi d_{ori}^2}{4}}$$

271 (Eq.13)

272 with d_{ori} the diameter of the orifice of the nozzle.

273 When writing Eq.9, the actual dioxygen concentration in the liquid was assumed to be null. To verify this
274 statement, the Hatta number was used to compare the rate of reaction and the rate of transfer:

$$275 \quad Ha = \sqrt{\frac{k [RSO] D_{O_2/H_2O}}{k_L}}$$

276 (Eq.14)

277 with k the reaction rate constant between O_2 and the DHR ($L \cdot mol^{-1} \cdot s^{-1}$), $[RSO]$ the concentration of dye
278 (mg/L). It is commonly accepted that the reaction does not accelerate the transfer measured when the Hatta
279 number is smaller than 0.3, as has been determined in several studies for resazurin dye (Yang et al., 2017).

280 **3.2 Procedure validation**

281 3.2.1 Optical window

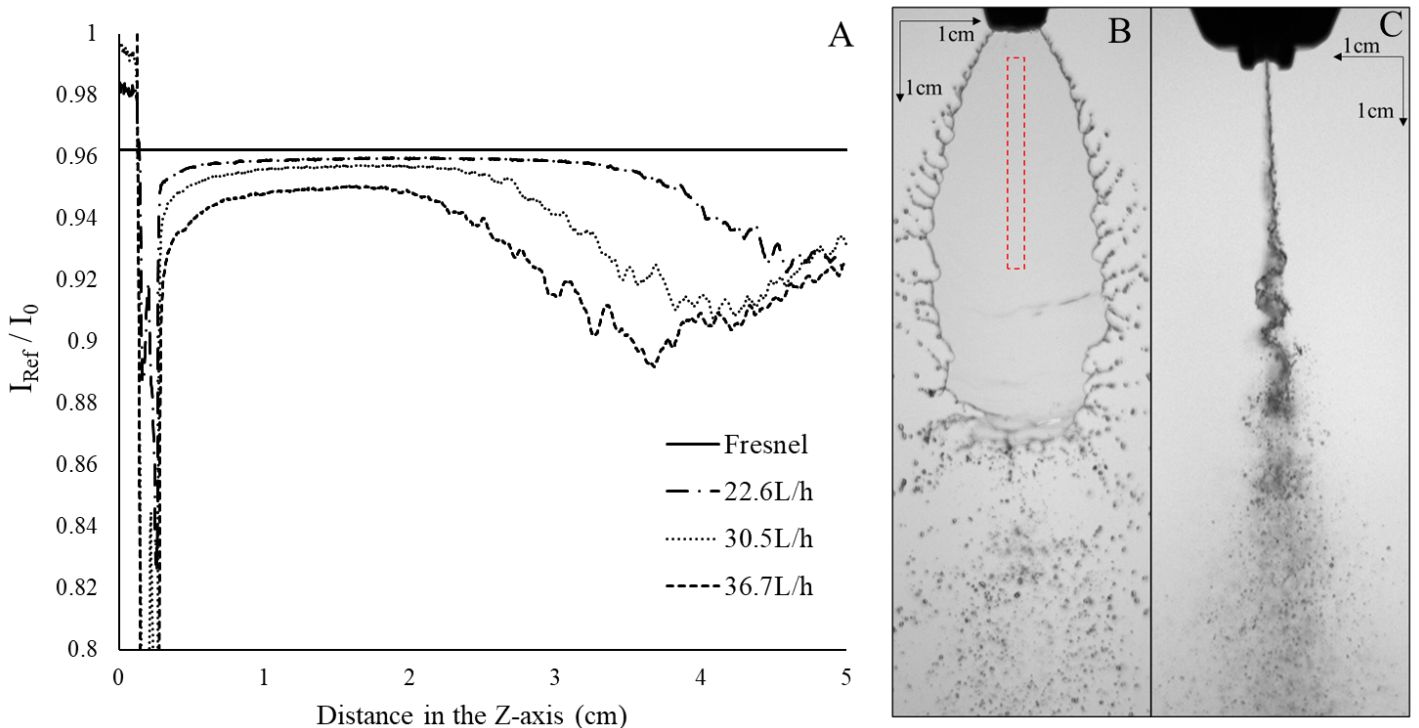
282 The first step of the method was to determine whether our optical system was consistent with optical
 283 theories such as the Beer-Lambert law. An optical theory that can be easily verified is the Fresnel Equation,
 284 which indicates the proportion of the light reflected at the interface of an optical medium. Considering a
 285 normal incidence of the light beams through a gas-liquid interface, the Fresnel equation (Träger, 2012)
 286 relates the intensity before the crossing of the interface to the intensity received after the reflection:

$$287 \left(\frac{I_{ref}}{I_0}\right)_{theoretical} = \left(1 - \left(\frac{n_{air} - n_{solution}}{n_{air} + n_{solution}}\right)^2\right)^2 \text{ (Eq.15)}$$

288 With n_{air} the optical index of the air ($n_{air}= 1$) and $n_{solution}$ the optical index of the solution ($n_{solution} = 1.33$).
 289 The latter correspond to the index of water at 20°C around 580nm. Note that this index should be slightly
 290 higher due to the presence of glucose in the solution (Weber, 2018).

291 By recording the background intensity I_0 received at the camera when no liquid was sprayed and comparing
 292 it with the I_{ref} , for the vertical study region (region 1), it was possible to plot the fraction of light intensity
 293 lost by the successive crossing of two gas-liquid interfaces (Fig.4A).

294



295

296 Fig.4: Ratio between the background intensity, I_0 , and the intensity I_{ref} recorded for the reference solutions

297 sprayed at different flowrates along the liquid film (A). Images with a larger acquisition window to fully
298 observe the liquid film from the front view (B) and side view (C). The red rectangle represents the largest
299 optical window obtained for the 22.6L/h flowrate.

300 Note that the strong variation obtained for the experimental curves in Fig.4a between $z = 0$ cm and $z = 0.3$
301 cm corresponds to the part of the image where the nozzle was located. As shown in Fig.4B and C, the light
302 did not cross the nozzle, so this area appeared black with low values of intensities. The ratio between the
303 two intensities varied considerably due to the noise of the camera in this region and the closeness of those
304 low values.

305 Moreover, in Fig.4A, the second part of the plot, from $z=3$ cm, also exhibited high discrepancies with Eq.15.
306 This was due to the increase of the amplitude of instabilities in the liquid film as shown in Fig.4C. In this
307 side view, it was possible to observe the increase of the amplitude of waves in the direction of the flow. As
308 can be seen in Fig.4B, dark folds appeared in the liquid, which caused a reduction of the intensity received
309 at the camera.

310 The instabilities then led to the breakup of the liquid film, and this breakup seemed to be described with
311 the decrease of the second part of the curves. This decrease occurred closer to the nozzle for high flowrates,
312 meaning that the liquid film produced at high flowrate was shorter. However, except at the beginning and
313 the end of the region of study, the experimental curves were in good agreement with Eq.15 and a normal
314 incidence of the light through the liquid film could thus be assumed. This hypothesis was essential for the
315 use of the Beer-Lambert law.

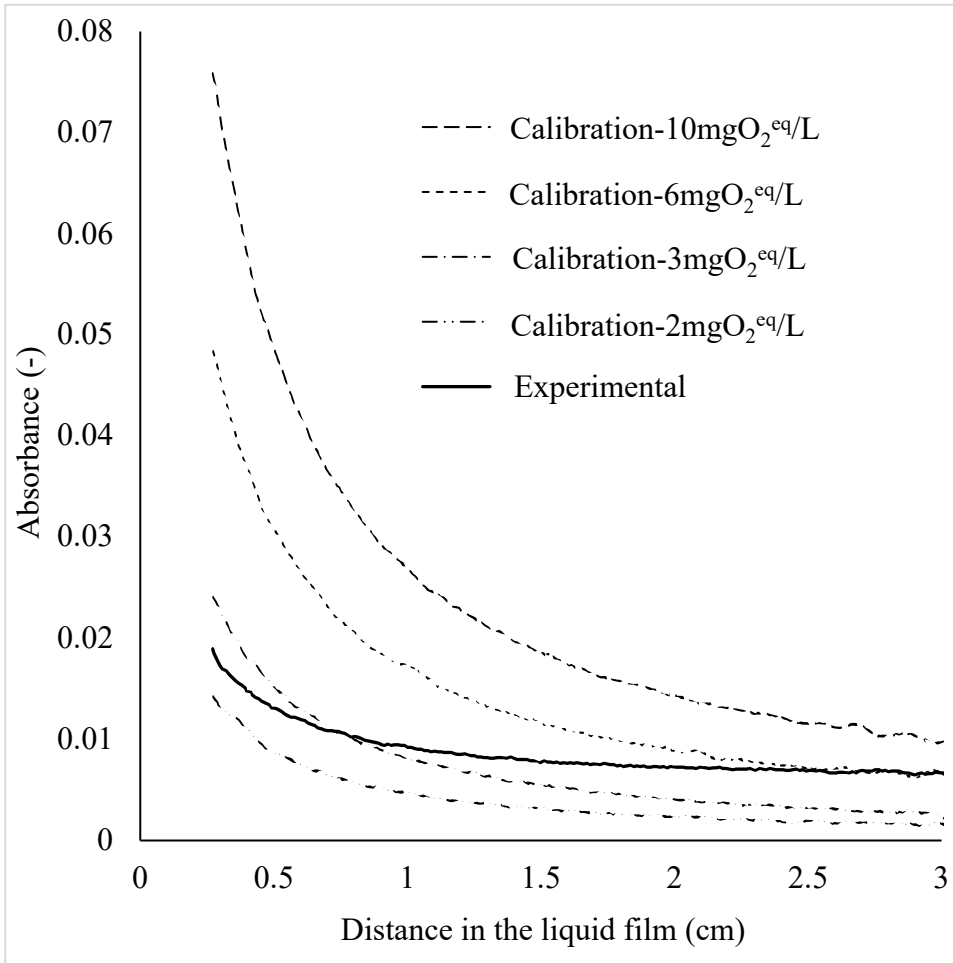
316 It then seemed necessary to consider an optical window in the images where optical theories were applicable.
317 For the present study, the optical window was defined as the part of the images where the difference between
318 the measured and theoretical I_{ref}/I_0 was lower than 1% for the 22.6L/h and the 30.5L/h flowrate. The
319 resulting optical window ranged from 0.3 cm to 2.9 cm in the liquid film for the 22.6 L/h flowrate, and
320 from 0.35cm to 2.5cm for the 30.5L/h. The higher flowrate, 36.7L/h, showed greater differences with the
321 Fresnel theory, the optical window was then defined for a difference of 2% with the theory, leading in a
322 optical window of [0.5cm – 2.0cm].For this reason, the following curves in the study did not start at zero

323 when describing an evolution inside the liquid film.

324 3.2.2 Absorbances & Beer-Lambert verification

325 Once the optical window had been determined for each flowrate tested, the absorbance profiles along the
326 z-axis in the liquid film could be determined according to Eq.1 and Eq.2. For a flowrate of 22.6 L/h, the
327 absorbances of the RSO solutions sprayed for a single run along region 1 have been plotted in Fig.5:

328



329

330 Fig.5: Absorbance profiles along the optical window for different RSO solutions sprayed with constant
331 concentration (calibration solutions) and for DHR solution (experimental) at 22.6L/h.

332 The Calibration-6 mgO₂^{eq}/L solution containing 120 mg/L of RSO had an absorbance profile higher than
333 the 3 mgO₂^{eq}/L solutions at 54 mg/L. The latter was also higher than the Calibration-2mgO₂^{eq}/L solution
334 with its 40 mgRSO/L, so, for increasing concentrations of dye, the absorbance also increased, consistently
335 with the Beer-Lambert law.

336 Absorbance profiles of the RSO solutions exhibited a common behavior: the absorbance decreased along

337 the liquid film. According to Eq.2, for a constant concentration of RSO, the only parameter acting on the
338 absorbance was the thickness of the liquid. Thus, the absorbance decrease observed in Fig.5 might be due
339 to a diminution of the thickness of the liquid film along the z-axis. This statement seems justified since
340 volume conservation of a bulk liquid implies that the thickness of the film decreases if its width increases,
341 as seen in Fig.4B.

342 Thus, before a quantitative study in terms of thickness or concentration variation could be performed using
343 the absorbance measurements, the Beer-Lambert law had to be demonstrated for the optical system.

344 *3.2.3 Beer-Lambert verification & RSO spectra*

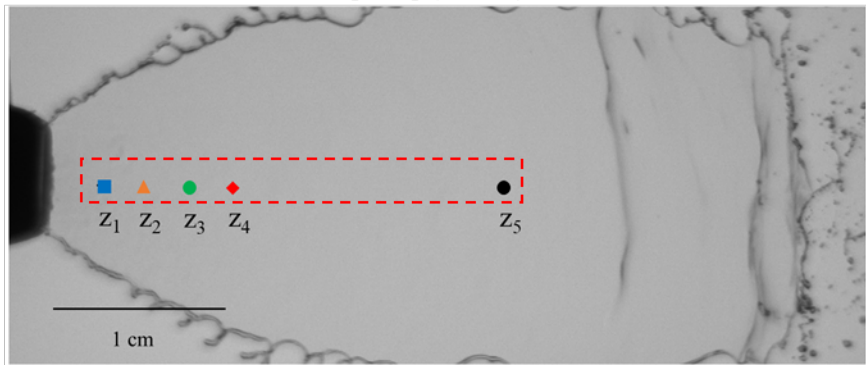
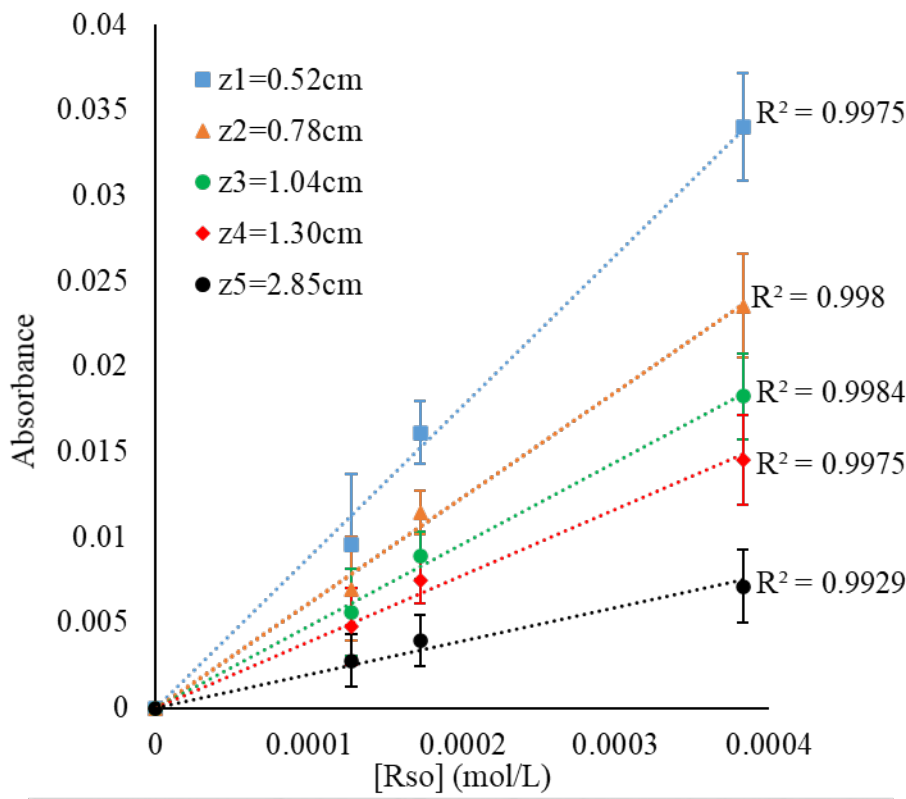
345 To verify the linearity of the Beer-Lambert law, it was necessary to associate the absorbance measurement
346 with known values of concentration and thickness. While concentrations were easily determined from the
347 mass and volume used for the preparation of the RSO solutions, the thickness of liquid crossed by the light
348 was unknown.

349 For a given flowrate, it was assumed that the nozzle produced a film with a given thickness profile.
350 Instabilities in the film induced the appearance of wavy motions in it and the waves were responsible for
351 local loss of intensity due to oscillations around the focal plane of the lens. They were also the origin of
352 deformations of the interface that perturbed the normal incidence of the light on the film. The spatial
353 occurrence of such instabilities was different from one image to another, so 500 images were averaged to
354 record a maximum of images without the occurrence of waves.

355 Considering the hypothesis put forward above, Fig.6 shows the absorbance measured at a given position
356 plotted against the concentration in RSO of the different solutions sprayed. For a position located 0.52 cm
357 from the border of the image (square in the photo of Fig.6), the evolution of the absorbance measured for
358 the 2, 3 and 6 mg/LO₂^{eq} solutions was linear. This linear correlation between absorbance and concentration
359 was also found for other positions in the liquid sheet, as shown for each slope in Fig.6. The observed
360 linearities validated the fact that the Beer-Lambert law could be used for our optical system. Note that the
361 10mgO₂eq/L solution did not respect the linear correlation, probably because of its high concentration in
362 resazurin, since the Beer-Lambert law is available for infinite dilution and without interactions between
363 solutes. For the remaining part of the study, the 10mgO₂eq/L solution was not considered.

364 According to Eq.2, the slope of the curves was the term $\varepsilon \times \delta(z)$. The slopes decreased with the distance
 365 into the film. Because ε is a constant property of the dye, the slope reduction can be explained by the
 366 decrease in thickness along the film. Thus, it is possible to conclude that the liquid film leaving the nozzle
 367 became thinner as it traveled further from the nozzle.

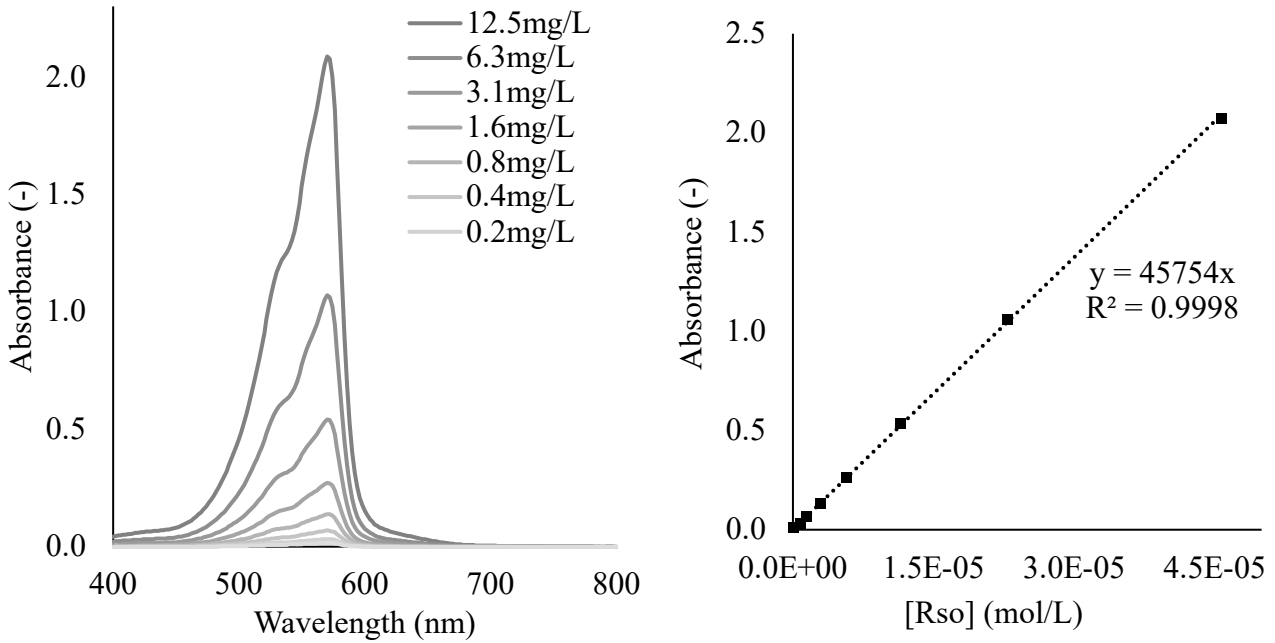
368



369

370 Fig.6: Absorbance of the sprayed RSO solutions versus their concentration for different positions in the
 371 liquid film for the 22.6 L/h flowrate in region 1 (top). The positions are indicated on the image of the
 372 liquid film with symbols and the red rectangle represents the optical window for the 22.6L/h flowrate
 373 (bottom).

374 The linearity between absorbance and dye concentration being proven, Eq.2 should be valid for making a
375 quantitative analysis of the thickness profile of the film using Eq.3. This implies the determination of ϵ .
376 The spectra in Fig.7 were obtained with a conventional spectrophotometer (Jasco V-630, Germany):
377



378
379 Fig.7: Resorufin spectra in the visible range using a spectrophotometer (left) and the corresponding
380 calibration curve at 572 nm (right).

381 The resorufin spectra presented in Fig.7 show a maximum absorbance at 572 nm. This was the reason why
382 the 550 nm filter was set up in front of the camera. It ensured that the camera received light that was likely
383 to be absorbed by the RSO. By measuring the absorbance of several diluted solutions at 572 nm, the molar
384 attenuation coefficient was determined to be around $45754 \text{ M}^{-1} \cdot \text{cm}^{-1}$ as shown in Fig.7. The maximum
385 wavelength and the attenuation coefficient found are consistent with those in the literature (Maeda et al.,
386 2000).

387 Finally, for the optical setup presented, a normal incidence through the liquid film can be assumed in a
388 defined optical window. This consideration allowed calibration curves to be plotted for the absorbance of
389 sprayed solutions of known concentration. The linearity observed between absorbance and concentration
390 at different places in the liquid film validated the possibility of using the Beer-Lambert law for quantitative

391 analysis of liquid thickness and concentration.

392 **4. Results**

393 *4.1 Hydrodynamic study*

394 *4.1.1 Qualitative observation*

395 Successive images of the liquid film acquired for different flowrates are represented on Fig.8. It was
396 observed that, for increasing flowrates, the angle of the liquid film (initially around 80°) became wider,
397 increasing the width of the liquid film.

398 This seems logical since the increase of the flowrate results in high inertial forces in the liquid (velocity
399 augment), but the surface tensions of the liquid remain constant as an intrinsic property of the fluid. The
400 surface tensions forces maintain the liquid as a continuous volume, but inertial forces, in addition with
401 friction, are in opposition of this phenomenon. The ratio between inertial force and surface tension increases
402 with the flowrate, then allowing the liquid to be more stretched, leading to width increase of the liquid film,
403 and growing instabilities.

404 The presence of folds in the liquid film was thus more frequent for the 30.5 and 36.7 L/h flowrates. As
405 shown in Fig.4A, the breakup of the film seemed to occur closer to the nozzle for those flowrates.

406

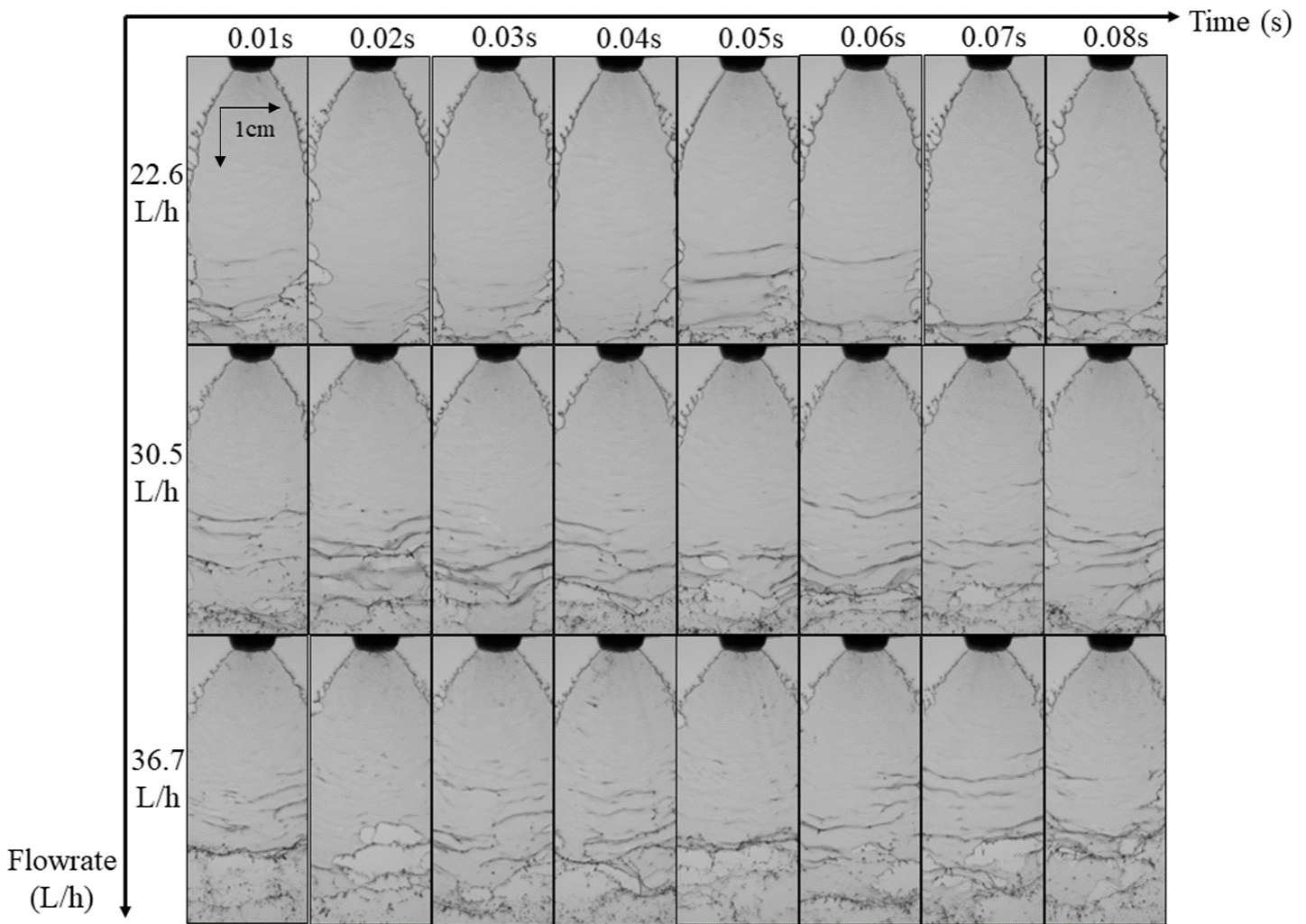


Fig.8: Images of the liquid film at different times for several flowrates.

Although instabilities were present at the bottom of the images for the 3 flowrates, the core of the liquid film seemed quite stable over time in its upper part since no patterns of waves were identifiable there from one image to another.

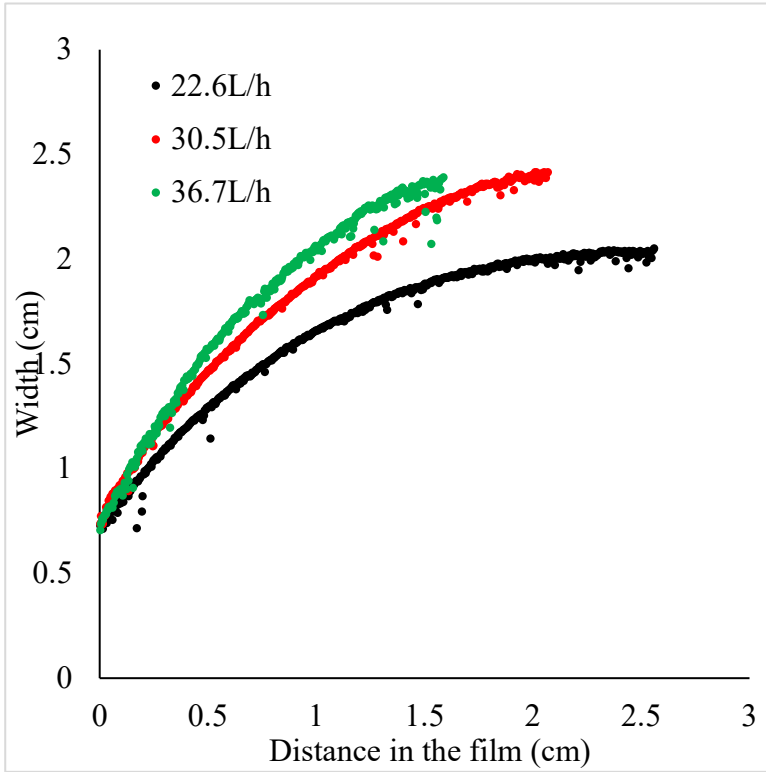
In all cases, the width of the film increased in the flow direction, until breakup occurred. This is consistent with the hypothesis of the thickness decrease along the z-axis as assumed in the procedure validation section. To respect volume conservation, it seems inevitable that an increase of the width of the liquid film should produce a diminution of the thickness. This qualitative observation can be quantified by image analysis.

4.1.2 Width profile

By using an edge detection algorithm to track the edges of the liquid film on 50 pictures with larger field of vision, the distance between the borders of the film can be determined and plotted along the flow direction as shown in Fig.9. The edge detection algorithm was not dependent of the optical windows defined

420 for the normal incidence of the light, then the measurement starts from the exit of the nozzle, directly when
421 the film is formed. Measurements are shown until the maximum width obtained, because after that the
422 algorithm fails to detect edges due to the presence of folds and breakup of the film.

423



424

425

Fig.9: Evolution of the liquid film width with the distance for 3 different flowrates.

426 This image analysis confirmed that the width of the film increased in the flow direction. The assumption
427 that the breakup occurred closer to the nozzle for increasing flowrates was also confirmed. For increasing
428 flowrates, the width profiles increased more rapidly but the breakup occurred earlier. For instance, with the
429 30.5 L/h flowrate, the width reached a maximum of 2.4 cm after an evolution of 2.5 cm along the film but,
430 for the flowrate of 36.7 L/h, the maximum width was reached after 2 cm in the film and was equal to 2.2
431 cm. It could have been expected that the maximum width for the 36.7 L/h flowrate would be higher than
432 that for 30.5 L/h but the breakup occurred before the width at 36.7 L/h exceeded that at 30.5 L/h. In all
433 cases, the width of the film expanded in the flow direction.

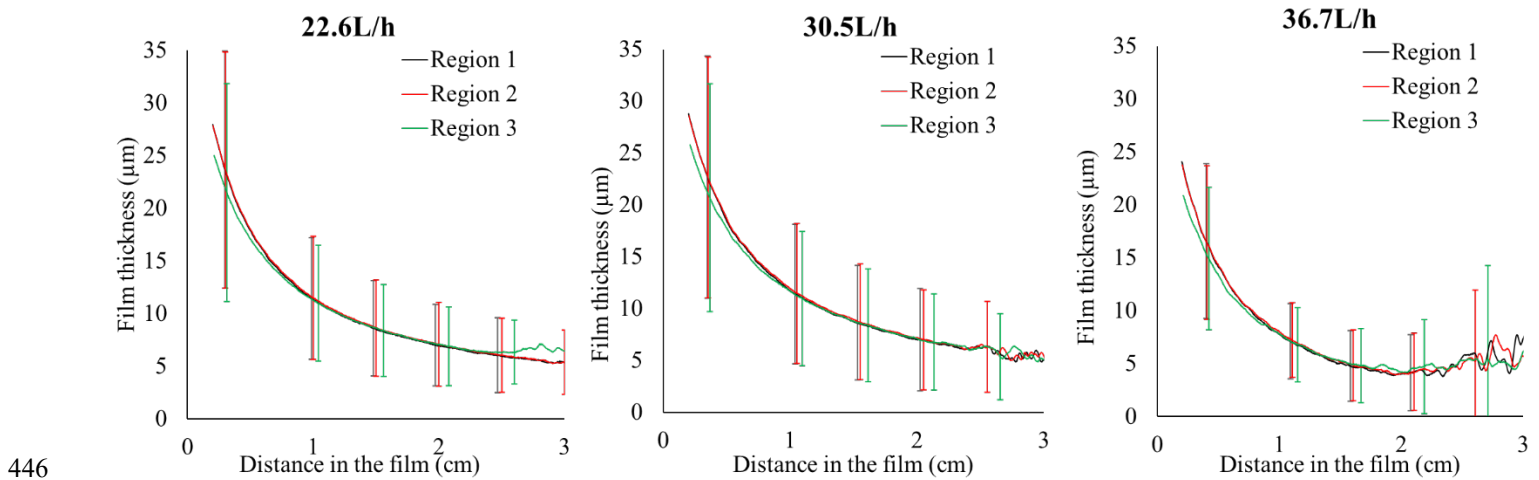
434 The different width profiles obtained in Fig.9 were integrated, from 0cm to their respective maximum width,
435 along the z-axis to evaluate the surface area of the liquid film produced for each flowrate, as proposed with
436 Eq.8. The area obtained for the 22.6 L/h flowrate was $8.51 \times 10^{-4} \text{ m}^2$ whereas, for the 30.5 L/h flowrate, the
437 liquid film surface area was $7.61 \times 10^{-4} \text{ m}^2$. An area of $5.63 \times 10^{-4} \text{ m}^2$ was obtained with the higher flowrate
438 of 36.7 L/h. The total liquid film surface as defined in Eq.8 becomes lower for increasing flowrates as

439 shown with the calculated values. Although higher widths are reached with higher flowrates, this surface
440 reduction probably results from an earlier breakup of the film due to the presence of more instabilities
441 motions in the liquid film for the high flowrates.

442

443 4.1.3 Thickness profile

444 From the different values of the RSO concentration and the molar attenuation coefficient ($454754 \text{ M}^{-1} \cdot \text{cm}^{-1}$)
445 ¹), the thickness profiles along the z-axis were determined using Eq.3. The profiles are plotted in Fig.10:



446

447 Fig.10: Thickness profiles along the liquid film for different flowrates and regions of study. Errors bars
448 are the standard deviation of the 18 (6×3) thickness profiles acquisitions (3 calibrations solutions per run).

449

For clarity, they are represented only for some points of the profile.

450 As assumed previously, the liquid film thickness decreased with increasing distance from the nozzle. From

451 around 30 μm at the outlet of the nozzle, the thickness of the liquid film reached values close to 5 μm after

452 a distance of a few centimeters. The thickness profiles of the 3 different flowrates exhibited the same

453 evolution. Note that the thickness profile for the 36.7 L/h seemed lower than for 22.6 and 30.5 L/h. Although

454 the width profiles were different for the 3 flowrates, the thickness profiles were quite similar for the three.

455 Note that we observed a surface reduction of the liquid film when increasing flowrates from the integration

456 of the width profiles, but the thickness profiles seemed not affected by the flowrate. Then, it was possible

457 to state that the volume of the liquid film produced by the nozzle decrease with increasing flowrates.

458 For each flowrate, the thickness profiles did not depend on the region of study. Region 1, which represented

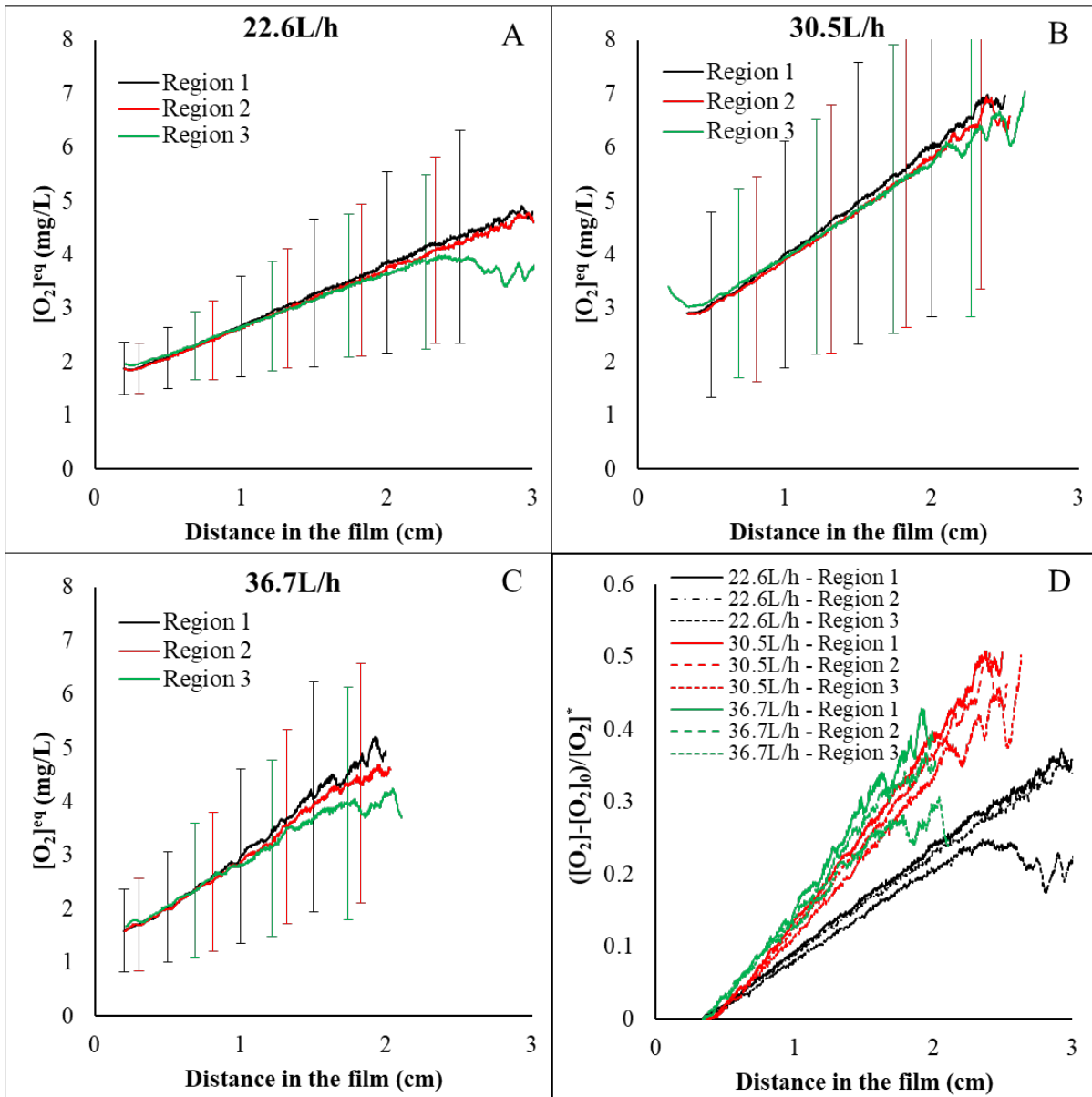
459 the vertical core of the liquid film, exhibited the same thickness profile as region 3. The latter described a
460 streamline between the core and the edges of the liquid film. Thus, it seemed that the liquid film offered a
461 relatively homogeneous thickness evolution. Note that the “distance in the film” refers to the actual distance
462 traveled on a given streamline, respecting the inclination of each region.

463 **4.2 Concentration measurements**

464 The goal of the concentration measurement was to quantify the transfer of atmospheric dioxygen to the
465 liquid film by observing the absorbance variation of the liquid film due to the sensitive dye. Once the
466 contribution of the thickness evolution to the absorbance variation in the liquid film had been assessed, the
467 appearance of RSO when spraying a DHR solution could be determined using Eq.4. The absorbance
468 A_{Exp} and the absorbances of the fully oxidized solutions A_{calib} are plotted in Fig.5.

469 The absorbance change along the liquid film for the experiment with DHR solution was produced by both
470 the oxidation of DHR into RSO and by the thickness variation. The absorbance evolution for the other
471 solutions was due only to thickness variation since the concentration of RSO was set constant by bubbling
472 before spraying. Thus, it was possible to see that the Experimental profile did not follow the same trend as
473 the other solutions because of the DHR oxidation and its corresponding change in concentration due to the
474 mass transfer phenomenon. The DHR curve crossed the 3 mg/L- O_2^{eq} and the 6mg/L- O_2^{eq} curves, denoting
475 the increase in RSO concentration in the film.

476 From the absorbance profile of the DHR solution and from the knowledge of the mean film thickness profile,
477 the equivalent dioxygen concentration that would have been present in the film is plotted in Fig.11(A, B,
478 C) using Eq.5. Note that no dioxygen was present in the liquid since the reaction of O_2 with DHR consumed
479 any molecule of O_2 that dissolved from the air to the liquid. In fact, production of an RSO molecule meant
480 that a dioxygen molecule from the gas had transferred to the liquid and then reacted with a molecule of
481 DHR. The equivalent dioxygen concentration on the y-axis represents the accumulation of dioxygen that
482 would theoretically occur if no reaction took place in the liquid.



483

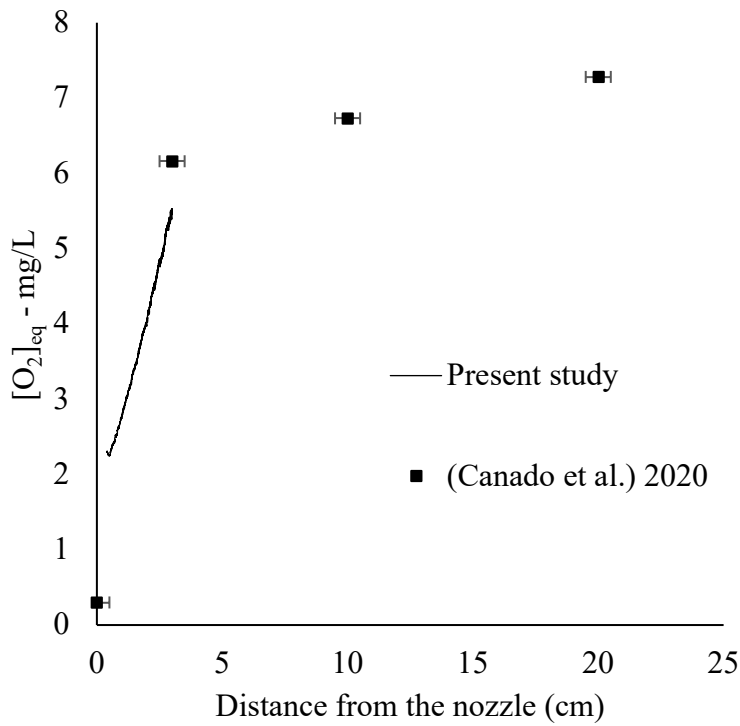
484 Fig.11: Equivalent dioxygen concentration profile along the liquid film determined by Eq.5 derived from
 485 the Beer-Lambert law. Errors bars represent the standard deviation of 6 acquisitions of the spraying of the
 486 experimental solution. For clarity they are represented only in some points of the profiles.

487 As expected, the dioxygen concentration increased in the liquid along the film as shown in Fig.11(A, B, C).

488 Since dioxygen was present in the gas phase and absent in the liquid phase, a strong difference in
 489 concentration existed and was favorable to the maximization of the driving force promoting the oxygen
 490 mass transfer. For the 22.6 L/h flowrate, the equivalent dioxygen concentration started at around 2 mg/L at
 491 the beginning of the optical window (0.3 cm into the film) and reached values around 5 mg/L after only 3
 492 cm in region 1.

493 For the 22.6 and 36.7 L/h conditions, the first concentration measured at 0.3 cm in the film was around 2

494 mg/L, while it was expected to be 0 since no transfer occurred before the spraying. The experimental
495 solution was probably oxidized by some adsorbed dioxygen present in the tubing between the nozzle and
496 the tank due to air leaks. In any case, as stated earlier, there was no dioxygen in the liquid since reaction
497 occurred in the bulk liquid. By removing the initial concentration of each curve and normalizing with the
498 saturation concentration $[O_2]^*$ it was possible to compare the evolution of equivalent dioxygen
499 concentration in the film due to the transfer of atmospheric O_2 for several conditions, as shown in Fig.11D.
500 The curves obtained seemed to show that the transfer was higher for increasing flowrates since the slope of
501 the respective curves were steeper as the flowrate increased. For the 22.6 L/h flowrate, the dioxygen
502 concentration reached around 35% of saturation after 3 cm in region 1, whereas this rate of saturation was
503 reached after only 2 cm with a flowrate of 30.5 L/h. It was also verified for the 36.7 L/h flowrate.
504 Comparison of the equivalent dioxygen profiles for 3 different regions in the film showed that the transfer
505 was not uniform in the liquid film formed during the spraying. For the 22.6 L/h flowrate, the concentration
506 was maximal for the core of the film, represented by region 1 in Fig.3, and it was weaker in observations
507 made closer to the edges of the film. In fact, the slope of the curve for region 1 was higher than that of
508 region 2, indicating a better transfer.
509 The profiles obtained for 30.5 L/h and 36.7 L/h flowrates were quite closer to each other than to the profile
510 for 22.6 L/h flowrate.
511 Although significant errors remained associated with the concentration measurement as shown in Fig.11,
512 the mean values obtained were consistent with the expected theoretical values: a liquid in equilibrium with
513 air at ambient pressure and temperature tends to reach a dissolved concentration of dioxygen of around 8
514 mg/L, as is the case in the literature, where experimental dioxygen absorption in a spray was performed by
515 liquid collection with a similar nozzle and flowrate (Canado et al., 2020). The global measurements
516 performed by liquid collection exhibited a strong increase in concentration between 0 and 3 cm of the spray.
517 After 3 cm, a smooth increase occurred, reaching the saturation value of 8 mg/L. The dioxygen
518 concentration profiles obtained in Canado's study and the present one have been grouped in a common
519 chart in Fig.12 to construct the evolution of the concentration in a whole spray:



520

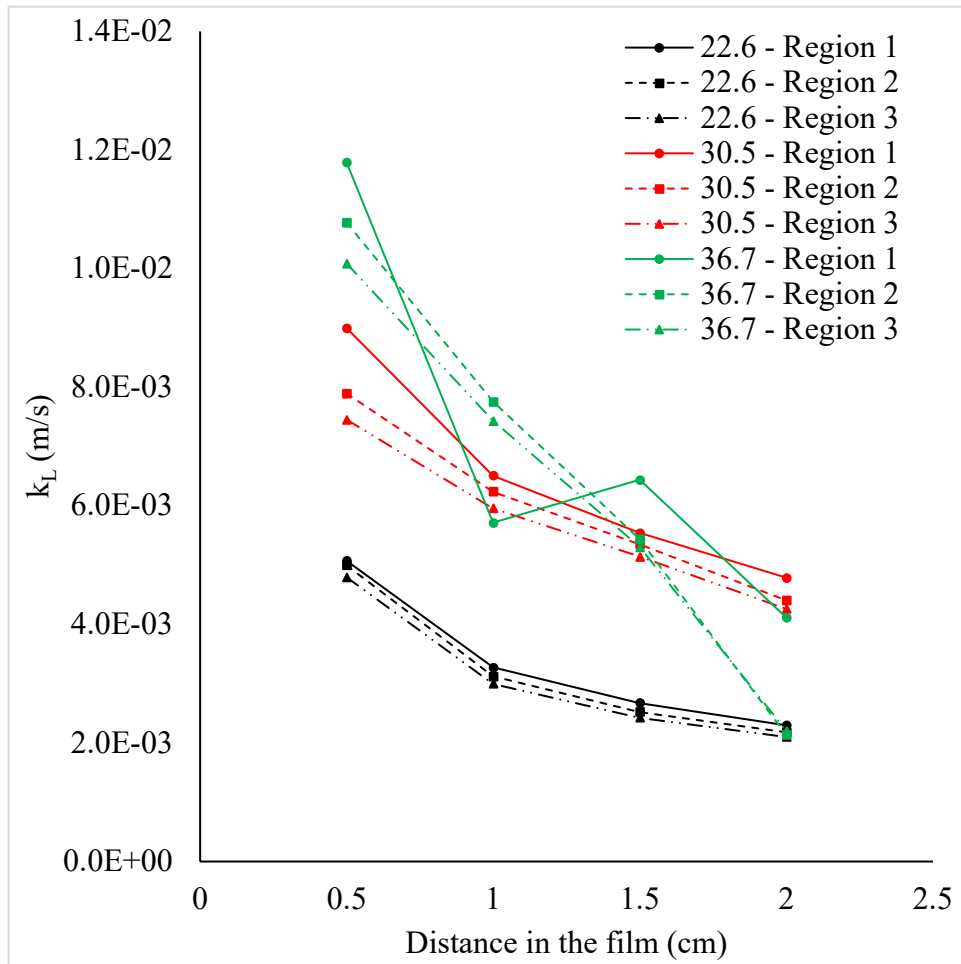
521 Fig.12: Dioxygen concentration profile obtained by liquid collection (squares) and with the present method
 522 (line) for experimental dioxygen absorption in a spray.

523 As stated in the introduction, liquid collection methods can suffer from end effects leading to an
 524 overestimation of the mass transfer occurring between two points of collection. The present method seems
 525 to fill the gap between the initial concentration at distance 0 and the concentration of the liquid collected 3
 526 cm downstream, as shown in Fig.12. Both methods highlight a considerable concentration increase by
 527 absorption in this region. Thus it is reasonable to attribute the experimental variation measured in this area
 528 to mass transfer. This comparison confirms that the mass transfer occurring in the first few centimeters i.e.,
 529 in the liquid film, was stronger than that occurring once droplets had formed. This transfer enhancement
 530 could be explained by a better interfacial area and hydrodynamics conditions of the liquid film region.

531 **4.3 Mass transfer analysis**

532 The liquid side mass transfer coefficient, k_L , denotes the strength of the transfer of a solute between two
 533 phases. Two approaches for the determination of this coefficient have been proposed. First, local analyses
 534 based on the evolution of the concentration pixel by pixel (i.e., $\frac{d[O_2]}{dz}$) for different positions in the film

535 were performed using Eq.9. This provided an accurate description of the evolution of the transfer along the
 536 film. Using Eq.10, a global analysis for a considerable section of the film (1.8 cm length) was performed
 537 to obtain a value of $\overline{k_L}$ able to represent the whole liquid film. The local analysis was performed for 3
 538 different flowrates and 4 positions, and the mean results are reported in Fig.13 and Table 2.



539

540 Fig.13: Local liquid side mass transfer coefficient determined with Eq.9 for different flowrates.

541 Fig.13 reports a common behavior of mass transfer, i.e. the increase of k_L with the velocity of the fluid.
 542 For a given cross section of the nozzle, increasing the flowrate leads to an augmentation of the velocity of
 543 the fluid. Thus, it seemed logical to see k_L increase with the flowrate. For each flowrate, region 1 exhibited
 544 higher values of k_L than regions 2 and 3, confirming a stronger transfer in the core of the liquid film than
 545 near the edges of the film.

546 The local analysis presented in Fig.13 and Table 2 allowed the decrease of mass transfer with distance in
 547 the film to be observed. For all the flowrates, high values of the mass transfer coefficient were determined
 548 at 0.5 cm in the film, whereas lower values were measured after 2 cm in the liquid film. For instance, at

549 22.6 L/h, k_L reached 5.1×10^{-3} m/s at 0.5 cm in the film, but it had half this value at $z = 2$ cm, with a value
550 of 2.3×10^{-3} m/s. This behavior was observed for all the regions and all the flowrates tested in the present
551 study. These results might express the deceleration of the liquid along the film since k_L is related to the
552 velocity of the fluid. The liquid exits the nozzle with a velocity of around 12.98 m/s as stated in Table.2,
553 and the velocities of the droplets have been measured at around 8.5 m/s in a previous study (Canado et al.,
554 2020) for a similar nozzle and flowrate, indicating a decrease in velocity of the liquid film from the orifice
555 to the formation of droplets. According to the shape of the orifice, the film spreads with a given geometry
556 and angle, and the friction with air causes instabilities to grow in its core and decrease its velocity, so it
557 seems consistent to attribute the decrease of the k_L with distance to the decrease of the velocity of the liquid
558 along the film.

559 Note that the results for the 36.7L/h seemed to dramatically decrease with the distance, especially for the
560 1.5 and 2cm distance, compared to the lower flowrates. It did not seem reasonable to attribute this behavior
561 to a mass transfer phenomenon but rather an uncertainty of measurement. Compared to the 22.6L/h and
562 30.5L/h flowrate, at 2cm, the dioxygen concentration profile for the 36.7L/h was not linear such as the two
563 other flowrates. The variations on this curve interfere with the calculation of dO_2/dz , that allow the
564 calculation of local k_L . Thus, the resulting k_L can be in contradiction with the ones determined for an almost
565 linear curve as the 22.6L/h and 30.5L/h dioxygen concentration profiles. Also, the optical window of the
566 higher flowrate was defined for 2% error with the Fresnel equation instead of 1% for the lower flowrates
567 in Fig.4.

Local analysis						
<i>Parameters</i>				<i>Region 1</i>	<i>Region 2</i>	<i>Region 3</i>
Q (L/h)	U (m/s)	z (cm)	w (cm)	$k_L \cdot 10^3$ (m/s)		
22.6	7.99	0.5	0.84	5.1	5.0	4.8
		1	1.38	3.3	3.1	3.0
		1.5	1.71	2.7	2.5	2.4
		2	1.91	2.3	2.2	2.1
30.5	10.79	0.5	0.93	9.0	7.9	7.5
		1	1.56	6.5	6.2	6.0
		1.5	1.99	5.5	5.3	5.1

		2	2.29	4.8	4.4	4.3
36.7	12.98	0.5	0.89	11.8	10.8	10.1
		1	1.69	5.7	7.8	7.4
		1.5	2.12	6.4	5.4	5.3
		2	2.35	4.1	2.1	2.2

568 Table 2: Values used for the calculation of k_L and the values of k_L determined with Eq.7.

569 The results of the global analysis presented in Table 3 confirm the increase of \bar{k}_L in the film with the
570 flowrates. The difference of transfer between the 3 regions of study is also confirmed, since the \bar{k}_L values
571 determined for region 1 are higher than those determined for regions 2 and 3. The global analysis provides
572 values of \bar{k}_L able to represent the whole liquid film and that can be used for the determination of
573 correlations for the mass transfer during the formation stage of the droplets by spraying.

Global analysis					
Z (cm)	Q (L/h)	\bar{w} (cm)		ΔC (mg/L)	$\bar{k}_L \cdot 10^3$ (m/s)
1.8	22.6	1.56	Region 1	1.98	2.8
			Region 2	1.91	2.7
			Region 3	1.79	2.5
	30.5	1.83	Region 1	3.10	5.0
			Region 2	2.99	4.8
			Region 3	3.02	4.8
	36.7	1.84	Region 1	3.44	6.6
			Region 2	2.96	5.7
			Region 3	2.52	4.9

574 Table 3: Values used for the calculation of \bar{k}_L and the values of \bar{k}_L determined with Eq.9.

575 From those global k_L and considering a reaction rate, k , of $1.28 \times 10^6 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ as stated in the literature
576 (Yang et al., 2016), the Hatta number was assessed at between 0.23 and 0.54. Hatta values under 0.3 mean
577 that the reaction between the O_2 and the dye does not accelerate the rate of transfer of O_2 from the air into
578 the liquid. Thus, it is possible to consider that the rate of transfer measured with the present method
579 corresponds to the actual rate of transfer occurring in the liquid film. In other words, the method does not
580 change the regime of transfer occurring in the liquid film.

581 Moreover, this means that no accumulation of dioxygen occurred in the liquid; it was instantly consumed
582 by the reaction.

583 No correlations are currently available in the literature for the formation stage of droplets during the

584 spraying. An effort has been made to plot the correlation between the mass transfer occurring in the liquid
585 film, denoted by the Sherwood number, and its hydrodynamics, expressed with the Reynolds number.

586

587 From the three different flowrates tested, a power law has been assessed to link the Sherwood and Reynolds
588 numbers based on the thickness of the liquid as the characteristic scale:

589

$$Sh = 0.0052 Re^{1.783}$$

590 Although the few conditions investigated here were not enough to perform a complete, rigorous mass
591 transfer analysis, the example of analysis given shows that it is possible to observe an acceptable correlation
592 ($R^2=0.995$) between the mass transfer and the hydrodynamics of the liquid film with the present method.

593 Commonly, such correlations for mass transfer with droplets or bubbles for steady flows propose a
594 Reynolds number with the power 0.5 (Codolo and Bizzo, 2013; Kumar and Hartland, 1999; Tanda et al.,
595 2011). The present correlation revealed a strong effect of the Reynolds number on the mass transfer since
596 the exponent found was equal to 1.783. This behavior has already been shown for mass transfer during the
597 breakup of a cylindrical jet (Srinivasan and Aiken, 1988). This result marked the importance of the flowrate
598 for the mass transfer in the formation stage of droplets compared to systems with settled droplets. The
599 present analysis had to be carefully considered since a small range of flowrates was tested because the
600 nozzle used had a reduced range of operating regime.

601 With this light absorption technique, it should be possible, in the future, to study the liquid film region to
602 propose several correlations between the mass transfer and the operating conditions. In addition with the
603 numerous existing methods for droplets characterization, the present method would allow a full description
604 of the mass transfer occurring in the spray, from the formation stage of the droplets (in the first centimeters)
605 to the cloud of droplets (as far as 1 meter downstream). The methods for liquid film and droplets
606 characterization complement each other to better understand the mass transfer occurring in sprays. Finally,
607 from the mass transfer analysis performed using dioxygen, the transfer for any solute in the liquid film can
608 be predicted with mass transfer theories.

5. Conclusions

A light absorption method has been successfully applied to measure the thickness of an atomizing liquid film. By using the dioxygen sensitive dye resazurin, the profile of dioxygen diffusing along this liquid film has been determined.

The liquid film was subject to growing instabilities that, once they reached a considerable amplitude, tore the liquid apart into droplets. The wavy motion induced by those instabilities produced dark folds in the film, leading to local losses of intensity. Despite that, the linearity of the Beer-Lambert law has been proven for different places along the film, allowing the thickness and concentration profile to be determined quantitatively. An example of mass transfer analysis has been presented to show the interest of the method. The latter analysis required concentration measurements that were performed thanks to the present method. This analysis led to the confirmation that the formation stage of the droplets enabled a higher mass transfer than the droplets once they were formed. A local analysis showed a decrease of the transfer along the distance of the film from the nozzle but also from the core of the liquid to the edges. Hatta numbers have been assessed from the mass transfer coefficient obtained and confirm that the present method correctly reports the actual regime of transfer occurring in the liquid film.

In the literature, mass transfer analysis of atomizing liquid film has commonly been global analysis performed by liquid collection and titration. The present method has the advantage of proposing a local analysis of the liquid film and the results are in good agreement with global studies. For the future, an effort must be made to challenge the method with different geometries of liquid film (conical, full conical, etc.), and flow conditions (flowrates/pressure), to propose correlations able to predict the mass transfer during the formation stage of the droplets.

Acknowledgments

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