Combining Global rainbow refractometry and PDA to extract the refractive index value by class of size:

Application to CO_2 capture by MEA spray.

S. Saengkaew*[1], M. Ouboukhil[2], L. Estel[2] and G. Gréhan[1]
[1] UMR CNRS 6614/CORIA, CNRS/INSA et Université de Rouen, FRANCE
[2] LSPC, INSA de Rouen, FRANCE
Sawitree_s@coria.fr, maria.ouboukhil@insa-rouen.fr,
lionel.estel@insa-rouen.fr and grehan@coria.fr

Abstract

For fundamental as well as industrial applications, the understanding of the thermo-chemical properties of sprays is a challenge, which necessitates physical modeling, numerical simulations and experimental approaches. The challenge of this particular experimental study is the possibility to measure the change of temperature and composition of droplets of Monoethanolamine (MEA) injected in an atmosphere charged in CO_2. When the MEA droplets react with CO_2, the droplets change of temperature and composition ($MEA+CO_2 \Rightarrow$ carbamate + heat), creating a change of the refractive index value of the droplets. To be able to optimize the capture of CO_2 by a spray of MEA, the efficiency of the chemical reaction by class of size must be measured. In this article, such a study is carried out by coupling global rainbow measurements and phase Doppler measurements (PDA). Then the technique is applied to measure the chemical extend of MEA droplets capturing CO_2 in order to determine the most efficient droplet size to optimize the CO_2 capture process.

Introduction

Nowadays, in order to limit the greenhouse effect, an important challenge is to reduce the quantity of CO_2 injected in the atmosphere. The reduction of the quantity of injected CO_2 can be obtain by combining different strategies as: favoring the use energy source as wind turbine or water turbine, nuclear plant, use of renewable combustible, improving the combustion efficiency of fossil combustible. Each of these approaches has advantage and disadvantage. Nevertheless, as all combustions produce CO_2, then the capture of the CO_2 after the combustion is critical. Capturing CO_2 can be carried out by using different technologies [1].

The CO_2 capture by MEA is often implanted in packing columns [2]. To increase the efficiency, a possible way is to increase the exchange surface between the liquid phase and the gas phase [3]. This increasing can be easily obtained by injecting a spray of MEA droplets in the gas [4]. However, to optimize the process, the optimal droplet size must be known. During the process of CO_2 capture, the droplet refractive index will evolve according with two phenomena:

- The heating of the droplet by the exothermic reaction will initiate a decreasing of the refractive index of the droplets
- The transformation of MEA in carbamate will initiate an increasing of the refractive index of the droplets

Then the value of the refractive index is a potential good indicator to quantify the chemical extends of the chemical reaction between the MEA and the CO_2. When the relationship between the refractive index, temperature and the chemical extend is known, the challenge is to measure the refractive index *in situ* in the droplet cloud.

To measure the refractive index of droplet, an attractive way is to measure the light scattered around the rainbow angle which codes both the droplet refractive index and the droplet size [5]. However, for individual droplet, the rainbow refractometry is difficult to use in realistic flow, as the signal is extremely sensitive to any change in the particle size, shape, refractive index. Then a more robust configuration must be used which is known as Global Rainbow Technique (GRT). The global rainbow technique has been first introduced by van Beeck et al [6]. The main principle of this approach is to record the light scattered in the rainbow direction by a large enough number of droplets, as in the nature. The resulting light distribution is still dependent on the value of the refractive index and on the size distribution then by using an appropriate signal processing the size distribution and an average value of the refractive index is obtained with a reduced sensitivity to the droplet shape [7, 8].

Then this paper is organized as follow. In the next section the extension of GRT to the measurement of the refractive index by class of size is introduced. In the third section, the relationship between the refractive index and the chemical extend and temperature is reported. In the fourth section, the experimental setup (including the reaction chamber) is described. Section five compiles some preliminaries results while section 6 is a conclusion.

---

[*] Corresponding author: sawitree_s@coria.fr

Numerical and Experimental Methods

Extension of Global rainbow technique to refractive index measurement by class of size: Numerical study

To validate the procedure proposed to extend GRT to refractive index measurement by class of size, a numerical simulation is used. Figure 1 displays an assumed size distribution. Figure 2 displays the assumed relationship between size and temperature which correspond to a relationship between refractive index and size, as temperature and refractive index are related by a linear relation. From these two information the synthetic global rainbow can be directly computed by using the Lorenz-Mie theory as shown in figure 3.

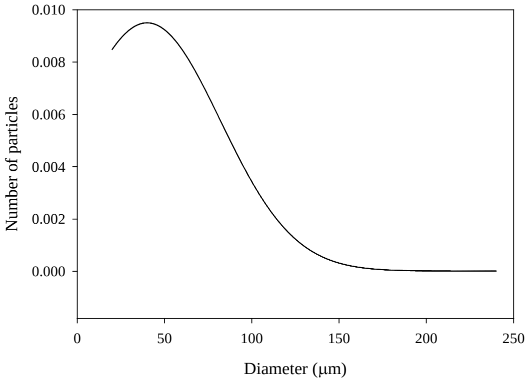


Figure 1 The assumed size distribution.

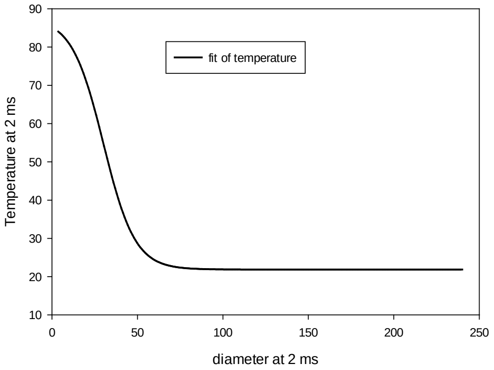


Figure 2 The assumed relationship between temperature (refractive index) and size.

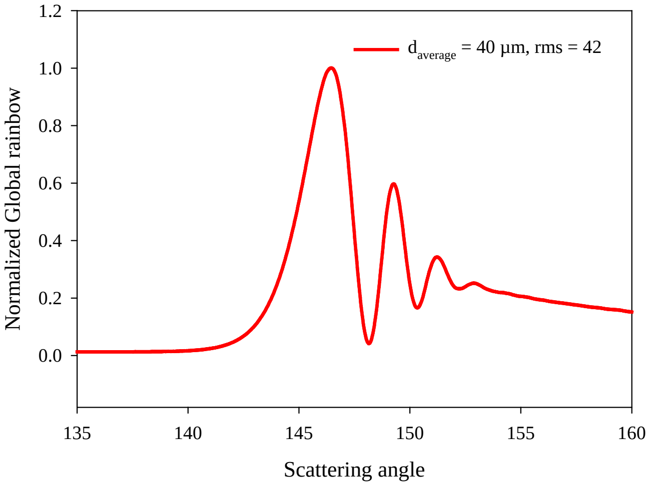


Figure 3 The computed global rainbow.

In a first step, this synthetic global rainbow is inversed by minimization, assuming that the size distribution is known as figure 1 and that the refractive index is a constant value. Then the extracted refractive index is obtained when the synthetic and recomputed global rainbow profiles are the most fitted. The best fit plotted as black spots is compared to the original global rainbow plotted as a continuous red line in figure 4.

In figure 4 three regions of the scattering diagram are identifiable: The main rainbow peak region, between 145 -147° where the agreement between the original global rainbow and the recomputed one is good. The feet region, below 145°, where the recomputed rainbow underestimates the original one and the tail region, scattering angle larger than 147°, where the recomputed rainbow smooth the original one.

In a second step, starting from the constant value extracted from the first step, the value of the refractive index is modified by class of size. The new values are qualified by increasing the minimization between the original rainbow and the recomputed rainbow. Refractive index values associated to small size act on the feet region while refractive index values associated to large size act on the tail region. The best fit is plotted in figure 5 as black spots. The agreement between the original global rainbow and the recomputed one is very good. Figure 6 plots the measured relationship between the refractive index and the particle size as black spots. The measured relationship fits the original one (plotted as red spots), excepted for the smallest diameters.

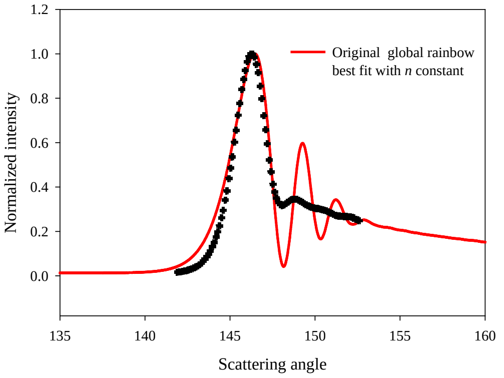


Figure 4 Comparison between the initial GR and the recomputed GR for a constant refractive index.

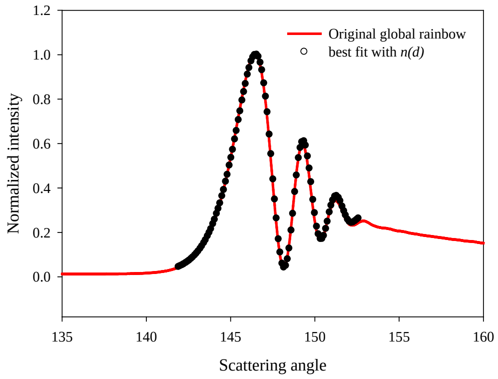


Figure 5 Comparison between the initial GR and the recomputed GR for a variable refractive index.

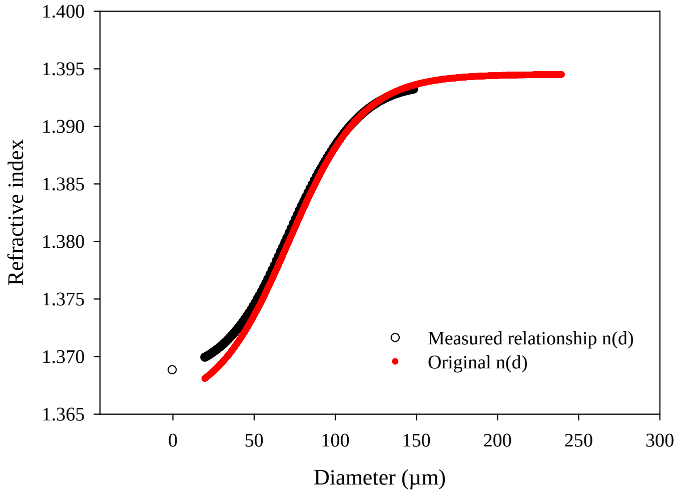


Figure 6 Comparison between the measured refractive index and the initial refractive index.

This section proves that when the size distribution is known, the relationship refractive index/size can be extracted from a recorded global rainbow. Then we have to select an optical method which can be considered as independent of the refractive index value comparatively to rainbow technique as holography, imaging, PDA and etc,. PDA is applied for this study.

Therefore, the next paragraph is devoted to quantify the sensitivity of PDA measurements to the refractive index values.

PDA sensitivity to refractive index value

In the framework of geometrical optics, in the forward direction, the scattered light is dominated by the refraction mode, leading to the following relation between the phase difference Φ and the particle diameter, for a PDA in classical configuration:

$$\Phi = C_1 D \tag{1}$$

The phase conversion factor C_1 is written as:

$$C_1 = 4\pi \left\{ \left[1 + m^2 - \sqrt{2} m \left(1 + \sin\frac{\theta}{2} \sin\Psi + \cos\frac{\theta}{2} \cos\Psi \cos\varphi \right)^{1/2} \right]^{1/2} - \left[1 + m^2 - \sqrt{2} m \left(1 - \sin\frac{\theta}{2} \sin\Psi + \cos\frac{\theta}{2} \cos\Psi \cos\varphi \right)^{1/2} \right]^{1/2} \right. \tag{2}$$

Where θ is the angle between the two laser beams, φ is the scattering angle, ψ the elevation angle and m the refractive index of the particles.

By using this relationship, it is possible to compute the answer for a typical configuration assuming that:

- The refractive index is constant and equal to the smallest refractive index value for the heating case (m = 1.370)
- The refractive index is constant and equal to the largest refractive index value for the heating case (m = 1.394)
- The refractive index is variable. It takes the value given in figure 2 in accordance with the diameter value.

The phase shift versus the diameter is plotted in figure 7 for these three cases with the following parameters: incident wavelength 0.532 µm, angle between the two beams $\theta = 4°$, scattering angle $\varphi = 45°$ and an elevation angle $\psi = 4°$.

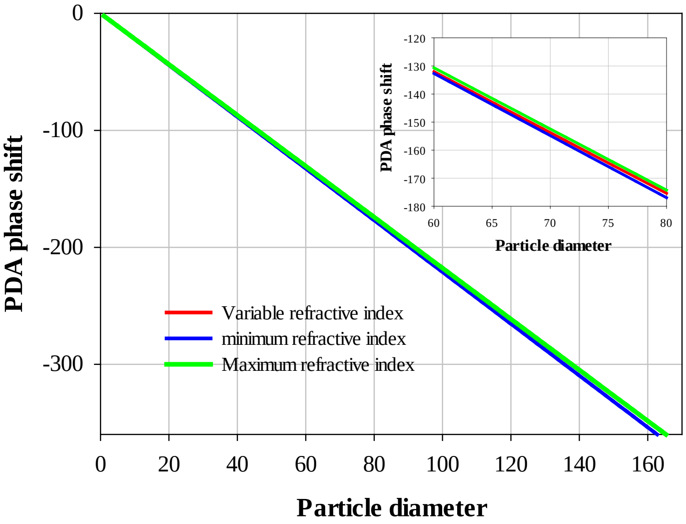


Figure 7 Relationship between phase shift and diameter. The parameter is the value of the refractive index.

These three curves are very close, the largest difference between measurements is less than 2 µm, assuming the smallest or the largest refractive index values. This result confirms that, at least for this configuration, PDA measurements can be assumed to be independent of the refractive index value of the droplets.

Global rainbow setup

The global rainbow setup used to record the global rainbow signal is shown in figure 8. The system consists of 1) a continue laser source from Dream Laser SDL-532-100T (wavelength: 0.532 µm, power: 200 mW) 2) a first collecting lens (diameter: 80 mm, focal length: 160 mm) which creates the image of the control volume on a spatial filter 3) a second lens (diameter: 80 mm, focal length: 200 mm) which creates an image of the image focal plane of the first lens on the detector. This optical arrangement permits to collect only the light scattered by the particles located in the control volume (1 mm^3) and organized by scattering angle 4) a CCD camera (Jai, 2048x2048 pixels, digitalization on 12 levels).

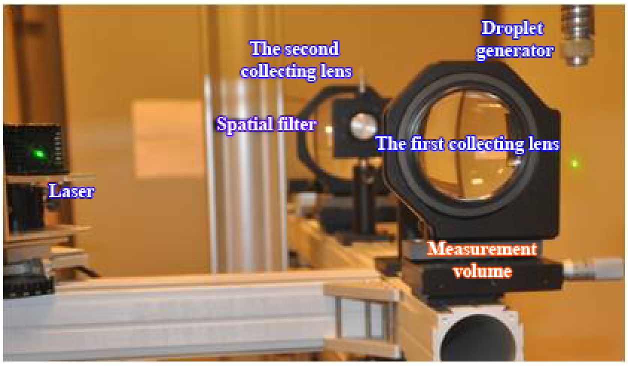


Figure 8 Global rainbow setup

Results and Discussion

Application of GRT and PDA to a real spray

The next step is to apply the technique to real experimental signal. Figure 9 displays a recorded global rainbow and a size distribution measured by PDA. Both have been recorded at the same position in a spray. Nevertheless, it must be noted than the global rainbow control volume is larger (1 x 1 x 1 mm) than the PDA control volume (200 µm^2 x 400 µm). The spray is realized by injecting n-octane droplets at 46.5°C in an ambient air at 26.5°C.

The results of these signals processing are plotted in figure 10. More accurately, in figure 10 three curves describing the value of the refractive index versus the diameter are plotted. The first one, plotted as a continue red line, corresponds to the value of the refractive index extracted from the global rainbow signal alone, by using a combination of non-negative last square and minimization to extract a size distribution and an average refractive index. The second one, plotted as a continue blue line, corresponds to the value of the refractive index extracted of the global rainbow by minimization using the measured PDA size distribution, assuming a constant value of the refractive index. Note that the both values are in good agreement. The third line, plotted as green spots, corresponds to the value of the refractive index extracted from the global rainbow signal by using the PDA size distribution with a minimization for each class of size. The fact that the refractive index value decreases from about 1.393 to 1.387, corresponds to the fact that the temperature of the small particles decreases faster than the one of the large particles. The black spots correspond to the temperature associated to the measured refractive index.

Figure 11 compares the experimentally recorded global rainbow plotted as a red continuous line to the recomputed rainbows. The continuous blue line corresponds to the recomputed global rainbow for the refractive index value extracted by using the PDA size distribution assuming a constant refractive index value, only the main peak is fitted. The continuous green line corresponds to recomputed global rainbow for a variable refractive index. The agreement with the measured rainbow is increases, especially for the tail of the signal.

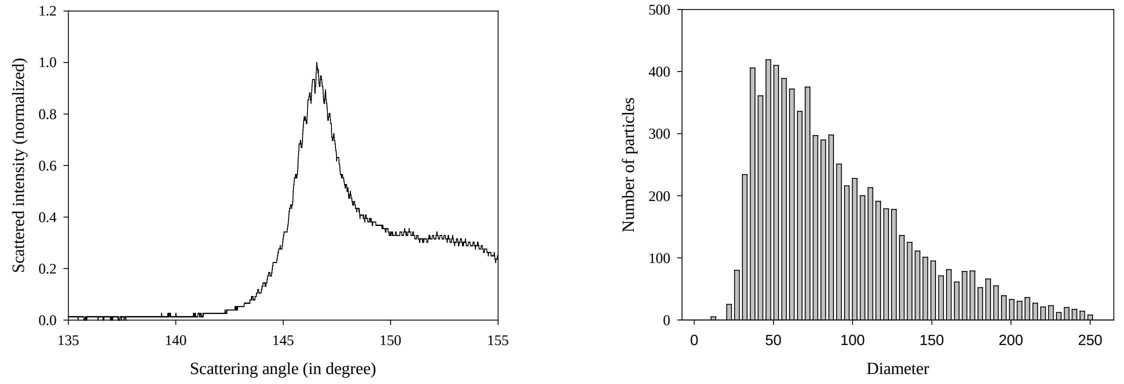


Figure 9 Experimental global rainbow and associated PDA size distribution.

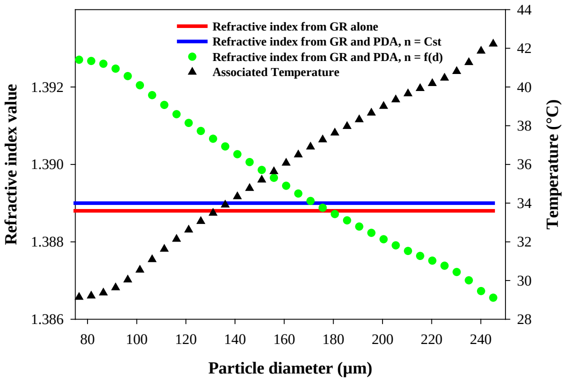


Figure 10 Measured refractive index (temperature) by class of size.

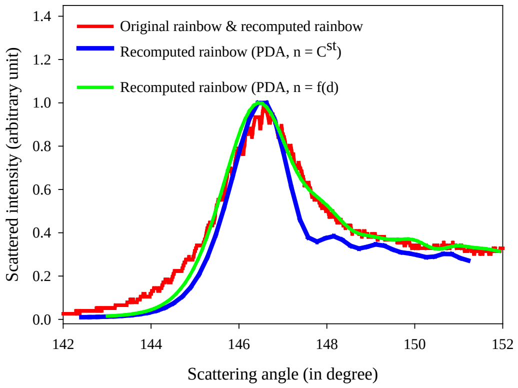


Figure 11 Comparison between the original and reconstructed global rainbow distribution

These results prove that the proposed method is also efficient to process real experimental signal. The next step is to apply the Global rainbow technique to the measurement of the CO$_2$ capture by MEA spray which is the aim of the next sections.

Relationship between refractive index and chemical extend

To measure the CO_2 capture by measuring the refractive index, first we must find a relationship between the refractive index value and the chemical extend of the reaction. This task has been carried out according with the following experimental scheme.

1. Solutions of MEA in water at 10, 20 30, 40 and 50% have been prepared.
2. These solutions have been saturated in CO_2.
3. Mixing of original solutions with saturated solutions has been realized to simulate various percentage CO_2 capture.
4. By using a refractometer, the refractive index of the solutions has been measured between 20 to 70°C.

As an example, Figure 12 plots the refractive index versus temperature and percentage of CO_2 captured for a mixing at 30% of MEA. From such figures, it is possible to define the sensitivity of the measurement of the chemical extend in terms of temperature and CO_2 per cent. From this view it is clear that the refractive index depends on the CO_2 concentration and temperature. As the CO_2 reaction with MEA is exothermic, the value of the measured refractive index will depends on both of CO_2 concentration and temperature. Nevertheless, the variation of refractive index is stronger with the variation of CO_2 than with the temperature.

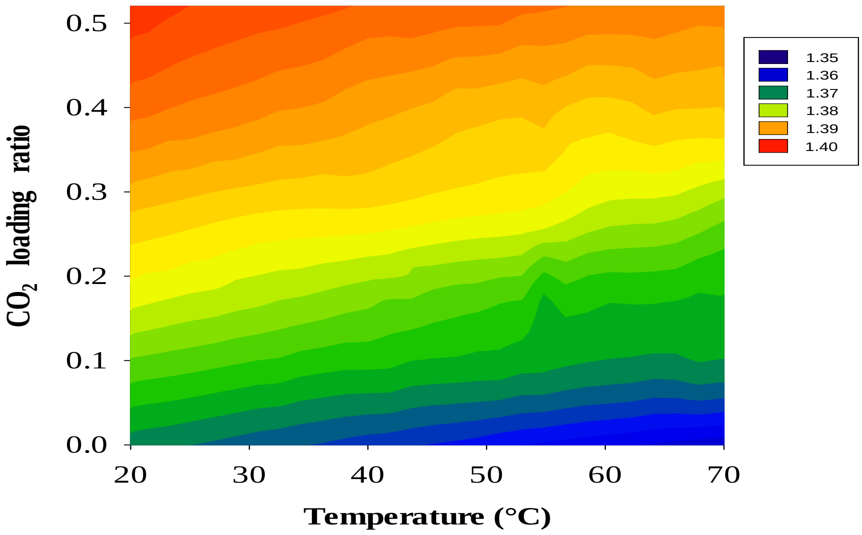


Figure 12 The refractive index value versus temperature and CO_2 content for 30%wt MEA.

These results show that the measurement of the refractive index is the measurement of the CO_2 capture with the accuracy of ±0.05 on the CO_2 loading ratio. The challenge is now to measure the refractive index in-situ in the spray. In this paper, the refractive index measurement will be carried out by using global rainbow technique.

Measurement of CO_2 loading ratio by using GRT in MEA spray

The MEA spray is created by an ultrasonic nozzle (40 kHz) producing droplets with an average diameter equal to 45 µm and a mean velocity equal to about 1 m/s. Preliminaries experiments have been carried out on sprays of monoethanolamine (MEA) solution in water at 30%, 40% and 50% and for the same initial solutions but after reaction with CO_2. Then, the global rainbow signal are recorded by the CCD camera and subsequently processed. The typical global rainbow images recorded by CCD camera for different MEA concentration without and with 100% of CO_2 are shown in figure 13. The sensitivity of the rainbow angular location to droplet composition is clearly visible on the recorded images. The rainbow angular location is shifted toward larger scattering angle when the concentration in MEA increases and when CO_2 is trapped in the MEA droplets. Figure 14 displays their extracted light distributions which are processed to extract the value of the refractive index as shown the measurement result in figure 15.

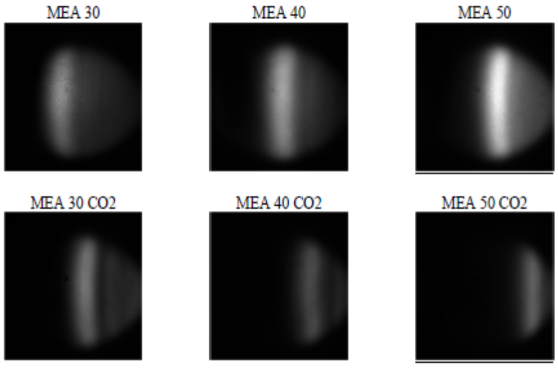


Figure 13 Examples of experimental global rainbow images. Top line pure MEA/water at 30, 40 and 50%. Below for fully load CO_2 in the droplets.

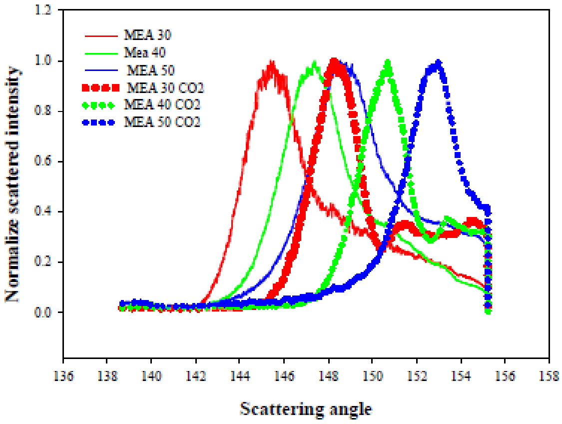


Figure 14 Global rainbow distribution associated to the global rainbow images of figure 12.

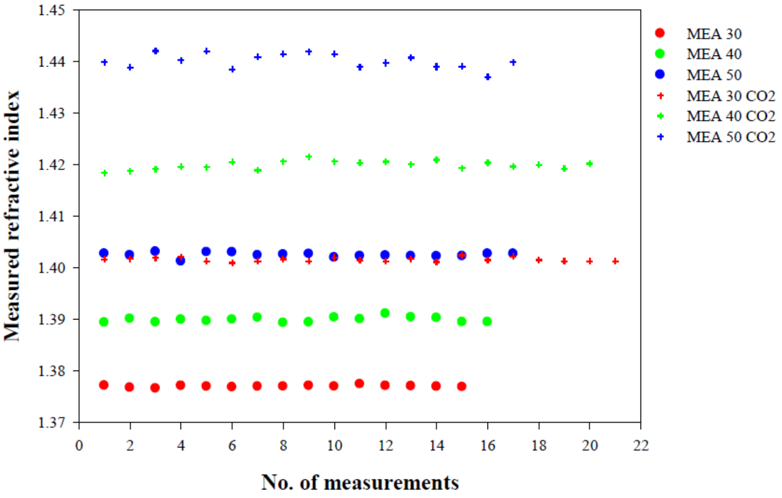


Figure 15 Droplets refractive index values measured by GRT for different MEA spray.

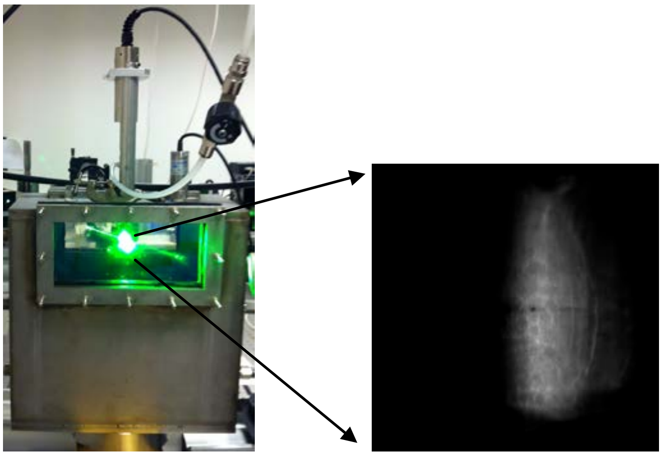
From figure 15, it can be concluded:

- The good stability of the measurements (the six series of experiments are essentially parallel)
- The good agreement between the refractive index values measured on the droplets by global rainbow refractometry and by classical refractometer.

Measurement CO_2 capture in the chamber

The previous results prove that GRT is well adapted to measure the MEA/water spray in free space. Consequently to be able to follow the dynamic of CO_2 capture by MEA spray a pressured chamber has been developed. The size of this chamber is equal to 150*300*300 mm. Optical accesses are assured by two glass windows 180*80 mm permitting to optically explore the top part of the chamber. On the top of the chamber is fixed the droplet generator (SONIC Vibra-cell, 40 kHz and 130 Watt). The chamber can be full up a mixing of N_2 and CO_2. A series of captor permits to measure the chamber pressure, the CO_2 concentration, and some others parameters.

A first series of experience has been carried out by using only the Global Rainbow Technique. The measurement point has been localized at 0.2 and 6 cm from the orifice of the droplets generator, on the mean axis. The MEA/water concentration is at 50%. Figure 16 displays a typical recorded global rainbow. This figure shows also that the droplet deposit on the window don't really affect the quality of the global rainbow measurements.



(a) (b)

F**igure 16**: a) the pressure chamber, b) recorded Global rainbow in the pressure chamber.

In this series of experiment only the zone close of the injector orifice has been explored. The results prove that, including for a chamber full of pure CO_2, the MEA droplets don't have the time to react with the CO_2. Then the injection will not be affected. The chamber is under modification to consequently increase the droplet path in the CO_2 gas.

Summary and Conclusions

In the study of two-phase flows, the understanding of the correlation between the droplet size and temperature and /or composition is a key parameter, as in the case of CO_2 capture by MEA sprays.

In this contribution a possible strategy to extend the global rainbow technique to such measurement has been introduced. First, we have numerically prove that if the size distribution is known by using and other technique as PDA, the processing of both signals (Global rainbow and PDA size distribution) gives access to the refractive index by class of size. Secondly, the method has been applied to experimental signals recorded on a spray of n-octane droplet under cooling. The next step is to apply the procedure to a spray of MEA capturing CO_2.

Acknowledgements

This work has been partially supported by the region Haute-Normandie (FRANCE) which grants M. Ouboukhil.

References

[1] R. Steeneveldt, B. Berger and T.A. Torp, CO_2 Capture and storage: closing the knowing-doing Gap, Chemical Engineering Research and design, 2006, 84(A9), 739-763

[2] I. Aouini, A. Ledoux, L. Estel, S. Mary, J. Grimaud and B. Valognes, Study of carbon dioxide capture from industrial incinerator flue gas on a laboratory scale, Energy Procedia, 4, 2011, 1729-1736

[3] A. Nuchitprasittichai and S. Cremaschi, Optimization of CO_2 capture process with aqueous amines using response surface methodology, Computers and Chemical Engineering, 2011, 35, 1521-1531

[4] J. Kuntz, A. Aroonvilas, Mass-transfer efficiency of a spray column for $C0_2$ capture by MEA, Energy Procedia, 2009, 205-209.

[5] N. Roth, K. Anders and A. Frohn, Refractive-index measurements for the correction of particle sizing methods, Appl. Opt., 1991, 30, 4960—4965

[6] J.P.A.J. van Beeck, Giannoulis, L. Zimmer and M.L. Riethmuller, Global rainbow refractometry for droplet temperature measurement, Optics Letters, 1999, 24, 1696-1698

[7] S. Saengkaew, Development of novel global rainbow technique for characterizing spray generated by ultrasonic nozzle, PhD thesis from University of Chulalongkorn (Bangkok, Thailand) and University of Rouen, 2006

[8] S. Saengkaew, G. Godard, J.B. Blaisot and G. Grehan, Experimental analysis of global rainbow technique: sensitivity of temperature and size distribution measurements to non-spherical droplets, Experiments in Fluids, 2009, 47, 839-848